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## **Chapter 2**

### **Portland Cement Clinker**



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## 1. CLINKER MINERALOGY

### 1.1 Theoretical Clinker Phases

The chemical composition (wt.%) of ordinary Portland cement clinker in the 'Holderbank' Group is on the average as follows:

Loss on ignition	0.48
SiO <sub>2</sub>	22.2
Al <sub>2</sub> O <sub>3</sub>	5.0
Fe <sub>2</sub> O <sub>3</sub>	2.8
CaO	65.4
MgO	1.8
SO <sub>3</sub>	0.54
K <sub>2</sub> O	0.63
Na <sub>2</sub> O	0.25
TiO <sub>2</sub>	0.27
Mn <sub>2</sub> O <sub>3</sub>	0.09
P <sub>2</sub> O <sub>5</sub>	0.14
Cl <sup>-</sup>	0.01
F <sup>-</sup>	<u>0.08</u>
	<u>99.70</u>

CaO<sub>free</sub> 1.3

With this knowledge it is possible to predict both:

- the phases which should theoretically be present in a cooled clinker of this composition
- the quantity of each phase which should be present.

For the given average chemical composition the potential mineralogy is calculated to be as follows:

C <sub>3</sub> S	=	54.3 %	C <sub>3</sub> A	=	8.5 %
C <sub>2</sub> S	=	22.8 %	C <sub>4</sub> AF	=	8.7 %

How was this calculation performed?

To predict the minerals which should potentially be present, the **phase equilibrium diagram** for the appropriate oxide system was consulted. Such diagrams are most easily located in the standard reference series 'Phase Diagrams for Ceramists' (Ref. 1).

To a first approximation the average clinker may be considered as consisting of only the three major oxides CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and hence its composition may be plotted using the well-known ternary phase diagram, CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub>. The given composition, i.e. 65.4 % CaO, 22.2 % SiO<sub>2</sub>, and 5.0 % Al<sub>2</sub>O<sub>3</sub>, when recalculated in terms of these three oxides alone, yields 70.6 % CaO, 24.0 % SiO<sub>2</sub>, and 5.4 % Al<sub>2</sub>O<sub>3</sub>, totaling altogether 100 %.

Consulting the CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> phase equilibrium diagram reproduced in a simplified formation in Figure 1, exhibiting only the **sub-solidous equilibrium relationships**, it can be demonstrated that the average composition \* lies within the C<sub>3</sub>S - C<sub>2</sub>S - C<sub>3</sub>A compatibility triangle.

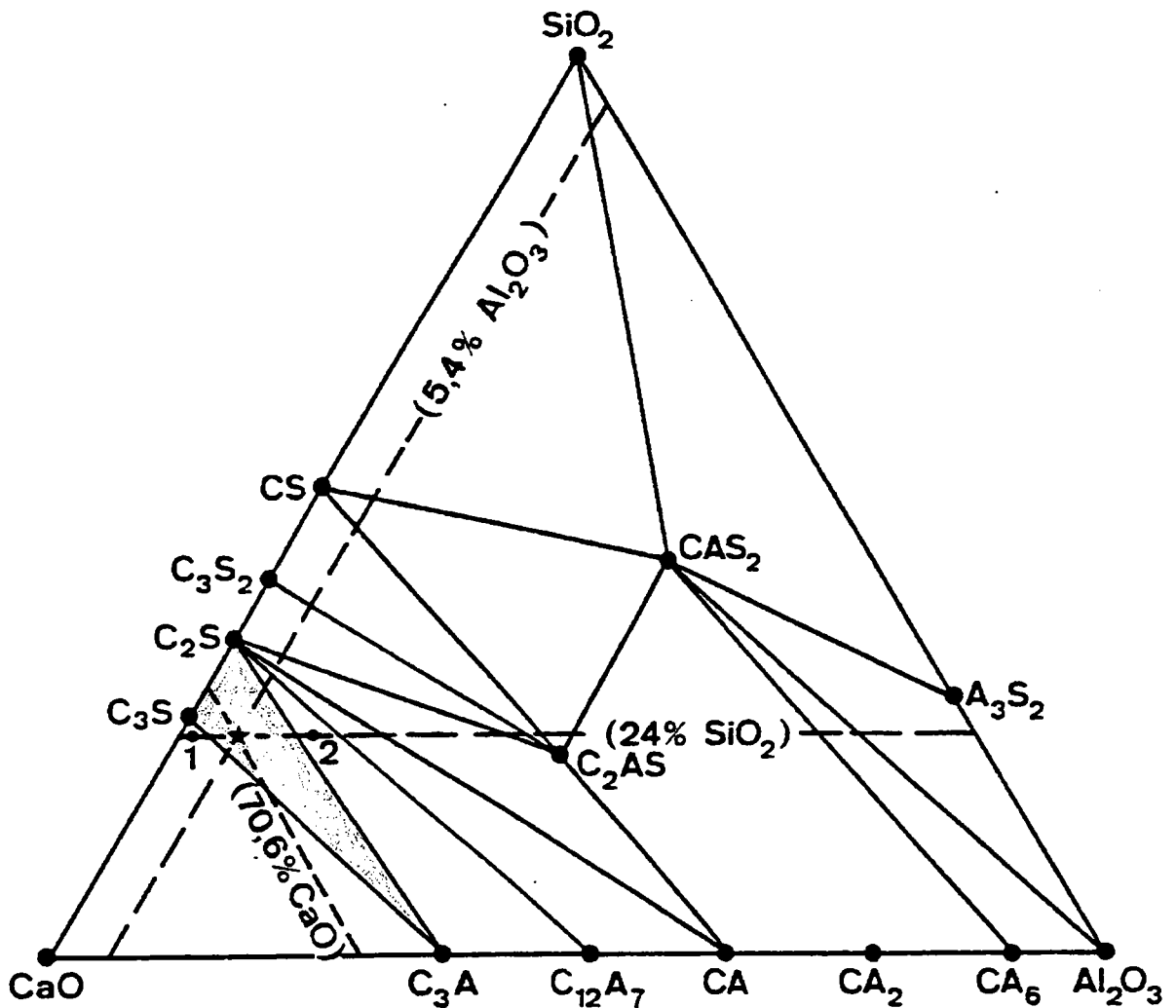
Because the chosen clinker composition lies within this triangle, these three phases will be formed on heating, provided that equilibrium is attained.

Small changes in the chemical composition of the mix are accompanied by changes in the **quantity** of the clinker phase C<sub>3</sub>S - C<sub>2</sub>S - C<sub>3</sub>A. As soon as the changes exceed a certain limit, different minerals are then formed.

Thus, if the SiO<sub>2</sub> composition is held constant at 24 % and the Al<sub>2</sub>O<sub>3</sub> reduced to 2 % (i.e. point 1 in Figure 1), the phases formed would be C<sub>3</sub>S - C<sub>3</sub>A - CaO, whereas increasing the Al<sub>2</sub>O<sub>3</sub> to 12.5 % (point 2 in Figure 1) would result in the formation of C<sub>2</sub>S - C<sub>3</sub>A - C<sub>12</sub>A<sub>7</sub>.

It can thus be realized why **maintaining the correct composition is important** in the production of Portland cement, and **why it cannot be varied over too wide a range**. Because only the three phases C<sub>3</sub>S - C<sub>2</sub>S - C<sub>3</sub>A possess the desired hydraulic properties, cement clinker composition should lie within the C<sub>3</sub>S - C<sub>2</sub>S - C<sub>3</sub>A triangle.

**Fig. 1: Sub-solidous phase equilibrium relationships in the system CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub>**

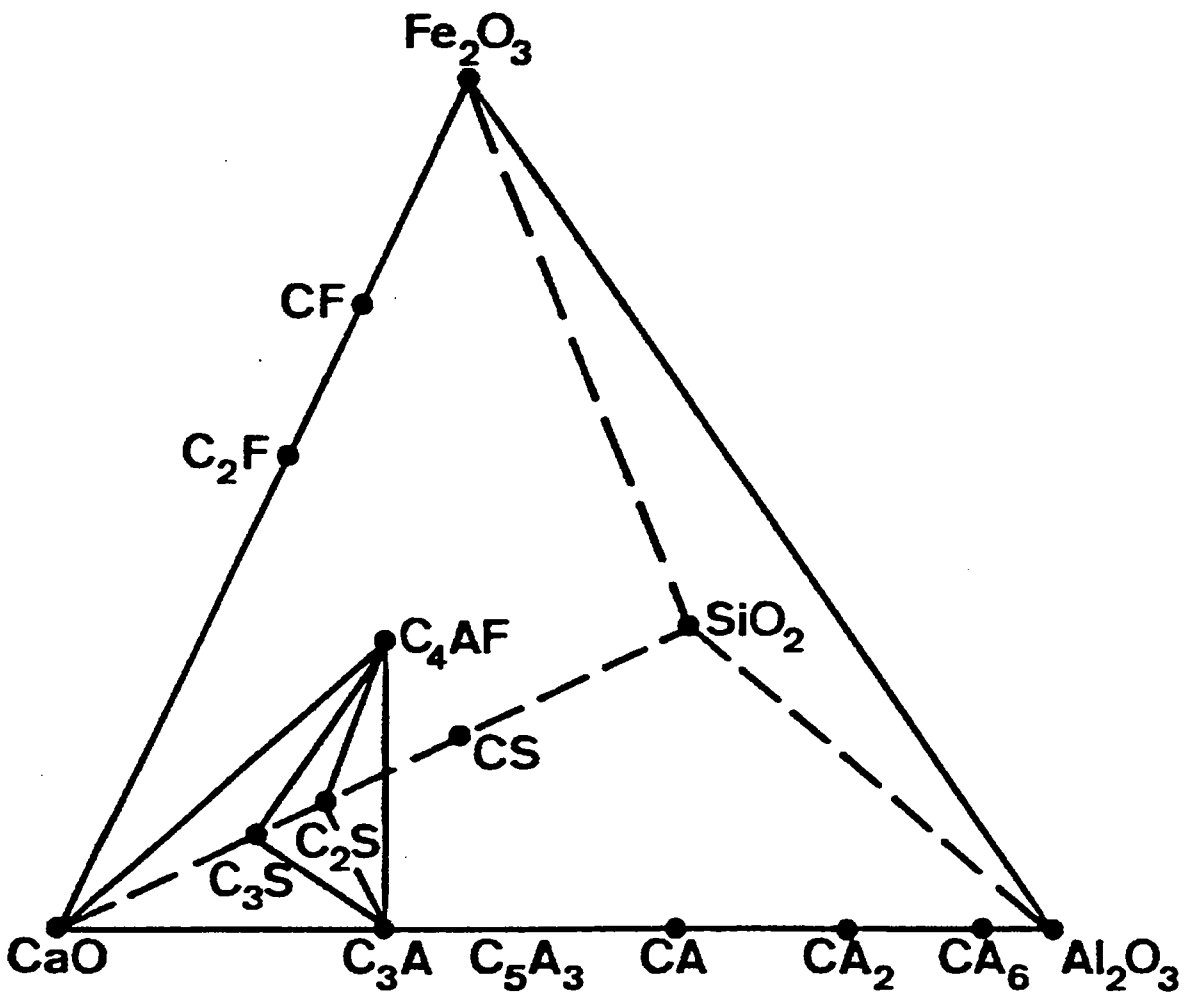


Clinker containing CaO - C<sub>3</sub>S - C<sub>3</sub>A would contain undesired free lime (responsible for expansion on hydration) while clinker containing C<sub>2</sub>S - C<sub>3</sub>A - C<sub>12</sub>A<sub>7</sub>, would contain no C<sub>3</sub>S, and would therefore exhibit unfavorable hydration and hardening characteristics.

A more accurate prediction concerning the theoretical phases present is obtained when the presence of Fe<sub>2</sub>O<sub>3</sub> is taken into consideration. On recalculation in terms of the 4 principal oxides, the composition of the so far considered average clinker becomes 68.5 % CaO, 23.2 % SiO<sub>2</sub>, 5.3 % Al<sub>2</sub>O<sub>3</sub> and 3.0 % Fe<sub>2</sub>O<sub>3</sub>, again totaling 100 %.

As in the case for CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub>, the above composition when plotted in the CaO - Al<sub>2</sub>O<sub>3</sub> - Fe<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> phase equilibrium diagram (Figure 2), shows the potential composition as lying within the C<sub>3</sub>S - C<sub>2</sub>S - C<sub>3</sub>A - C<sub>4</sub>AF compatibility volume and hence consists of these phases.

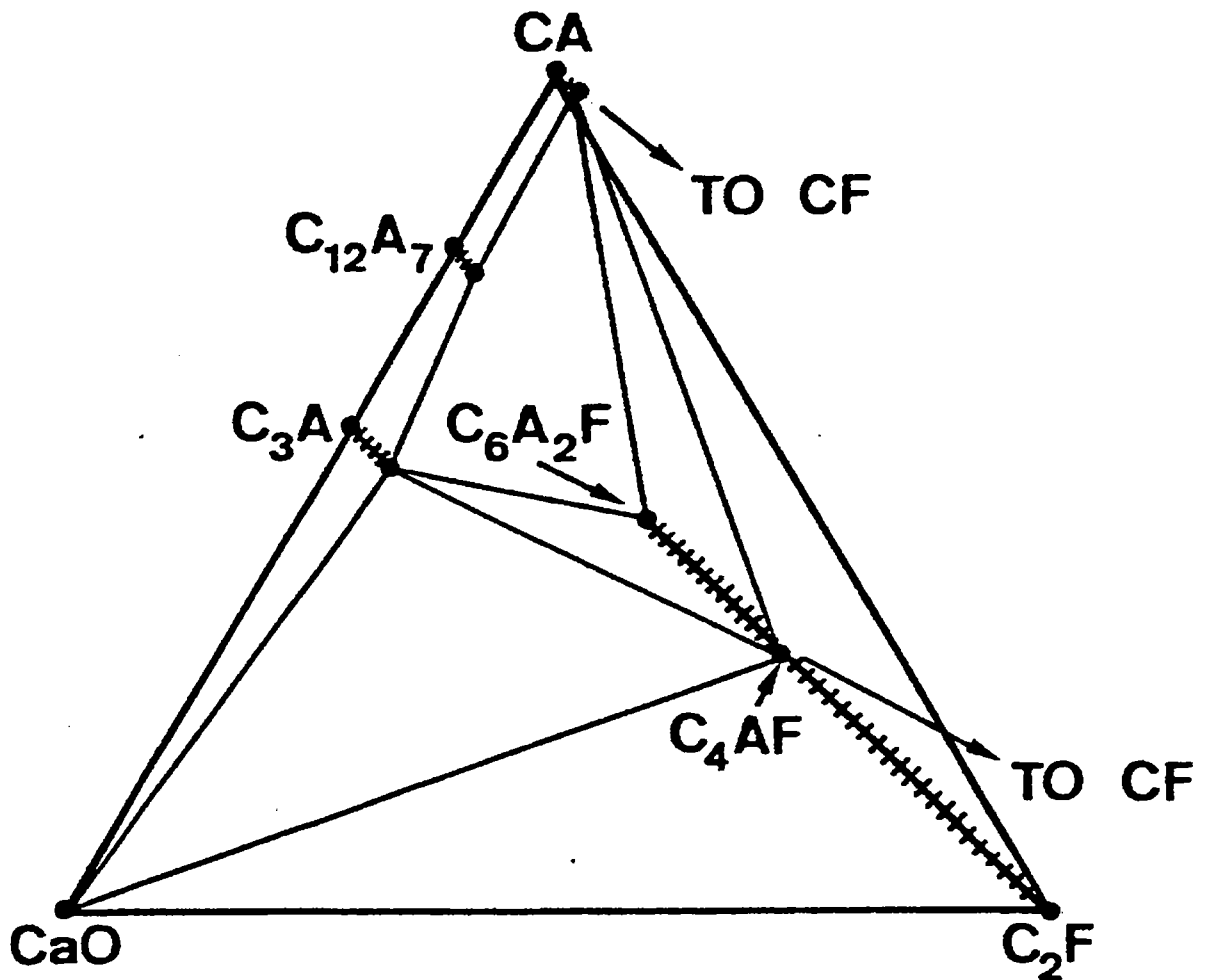
**Fig. 2: Sub-solidus compatibility relations in the system CaO - Al<sub>2</sub>O<sub>3</sub> - Fe<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub>**



A point of special interest here is that three of the phases C<sub>3</sub>S - C<sub>2</sub>S - C<sub>3</sub>A are binary compounds, i.e. composed of only two oxides. The other phase C<sub>4</sub>AF is a ternary oxide, composed of CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. Although C<sub>4</sub>AF is often considered as being an individual compound of fixed composition, it is in reality a member of the solid solution series 2 CaO · Fe<sub>2</sub>O<sub>3</sub> - 'CaO · Al<sub>2</sub>O<sub>3</sub>' in which 50 % of the Fe<sup>3+</sup> atoms are replaced by Al<sup>3+</sup> atoms, hence giving the composition 2 CaO · 1/2 Al<sub>2</sub>O<sub>3</sub> · 1/2 Fe<sub>2</sub>O<sub>3</sub>, i.e. 4 CaO · Al<sub>2</sub>O<sub>3</sub> · Fe<sub>2</sub>O<sub>3</sub>.

This solid solution series can be clearly seen in Figure 3, running from composition  $2 \text{CaO} \cdot 1/2 \text{Al}_2\text{O}_3 \cdot 1/2 \text{Fe}_2\text{O}_3$  to the end member of approximate composition  $6 \text{CaO} \cdot 2 \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ , i.e.  $\text{C}_6\text{A}_2\text{F}$ , in which 2 out of 3  $\text{Fe}^{3+}$  atoms have been replaced by  $\text{Al}^{3+}$ . The theoretical end member with 100 % replacement of  $\text{Fe}^{3+}$  by  $\text{Al}^{3+}$ , i.e. ' $\text{C}_2\text{A}$ ', is not stable at normal atmospheric pressure, but only at pressures in the order of 15000 bars.

**Figure 3** Phase equilibrium diagram of the portion  $\text{CaO} - 2\text{CaO} \cdot \text{Fe}_2\text{O}_3 - \text{CaO} \cdot \text{Al}_2\text{O}_3$  of the  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  system



In the already mentioned average clinker the oxides  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ , total 95.6 %, the remaining 4.4 % being principally composed of  $\text{MgO}$  (1.8 %), the alkalis  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  (0.9 %) and  $\text{SO}_3$  (0.5 %). These **minor oxides** not only are located within the lattices of the  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$ , (as will be demonstrated later) but also exist in the clinker as free  $\text{MgO}$  (periclase) and as alkali and alkali/calcium sulfates.

## 1.2 The Real Clinker Minerals

We are now acquainted with the clinker phase from the theoretical point of view, but what are the real chemical compositions of the clinker minerals?

Except for periclase (MgO) and free lime (CaO), all clinker minerals are **solid solutions**, i.e. they occur as single crystalline phases which vary in composition within finite limits without the appearance of an additional phase. The 'pure' compounds  $C_3S$ ,  $C_2S$ ,  $C_3A$ , thus, do not occur in this simple form, but contain a whole series of oxides such as **MgO, Na<sub>2</sub>O, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>**.

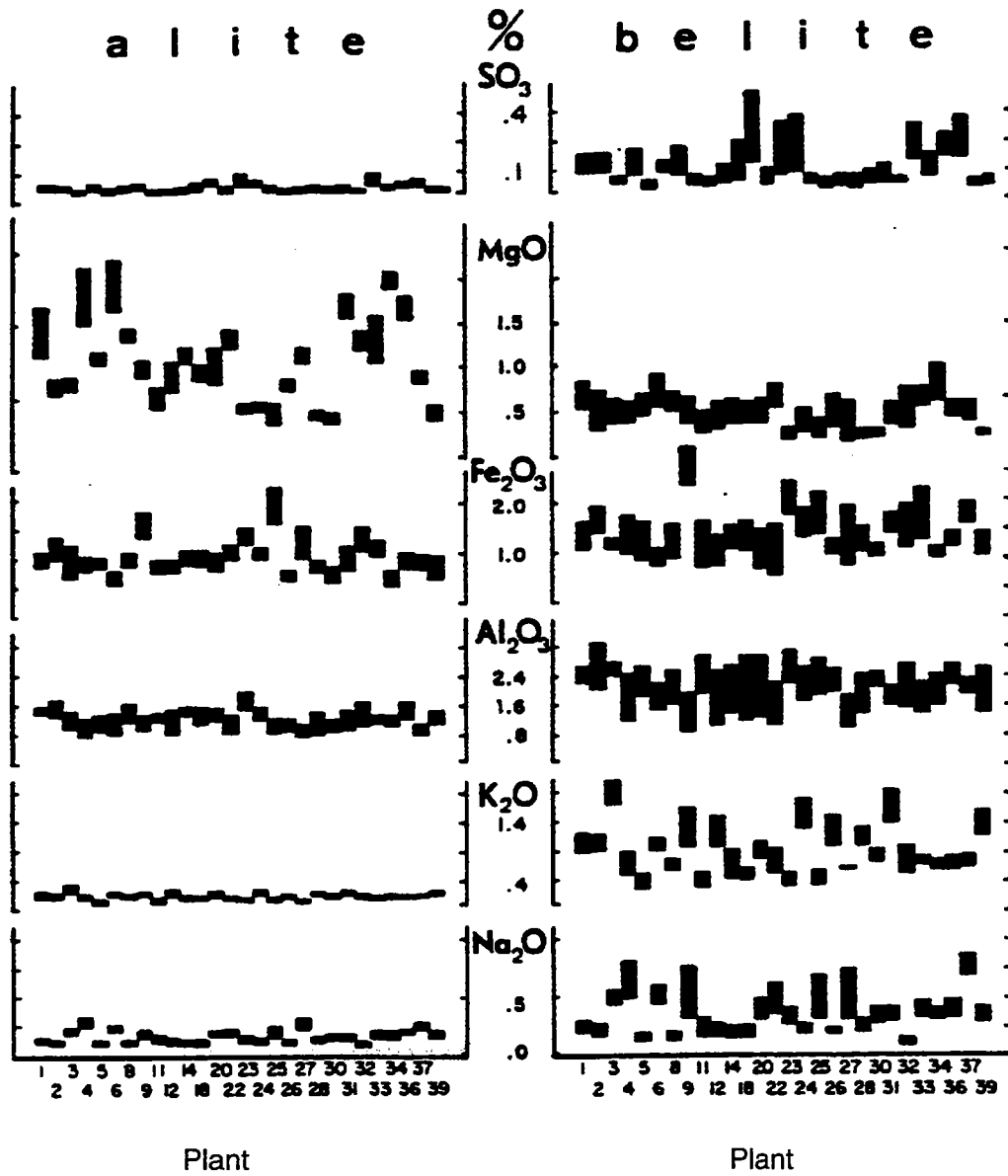
Whereas for the pure phases we use the abbreviations  $C_3S$ ,  $C_2S$ , etc., for the real minerals only the names **alite, belite, aluminate and ferrite** should be used.

Until the development of extremely sophisticated analytical techniques (electron microprobe analyzer and energy disperse analyzer), the determination of the maximum quantities of these minor oxides that could be incorporated into the 4 principal clinker minerals was based on laboratory experiments using the pure theoretical phases  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$ . The quantities actually present, i.e. the true distribution of the oxides, remained unknown. By using the microprobe technique, however, it is now possible to determine the range of composition of even the individual alite, belite, aluminate and ferrite crystals in any factory produced clinker.

In a recent study (2), based on 28 clinkers from 'Holderbank' Group plants, it was found by electron microprobe analysis that the range of MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O and Na<sub>2</sub>O present in the alite and belite crystals varies from plant to plant (see Table 1 and Figure 4). Moreover, even within one particular clinker grain, the individual alite and belite crystals show varying minor element incorporation.



Figure 4 Wt % chemical variation ( $\square \pm s$ ) of MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and Na<sub>2</sub>O in alites and belites in various cement plants



**Table 1 Real clinker minerals: chemical variation between different plant clinkers**

	Alite			Pure C <sub>3</sub> S	Belite			Pure C <sub>2</sub> S	Aluminate			Pure C <sub>3</sub> A	Ferrite			Pure C <sub>4</sub> AF
	min.	max.	$\bar{X}$		min.	max.	$\bar{X}$		min.	max.	$\bar{X}$		min.	max.	$\bar{X}$	
SiO <sub>2</sub>	24.4	25.9	24.5	26.31	29.8	32.9	31.3	34.88	3.1	4.3	3.9		1.8	3.1	2.5	20.98
Al <sub>2</sub> O <sub>3</sub>	1.0	1.8	1.3	-	1.5	2.8	2.2	-	28.7	31.8	30.8	37.74	20.2	24.4	22.5	32.86
Fe <sub>2</sub> O <sub>3</sub>	0.4	1.7	0.8	-	0.7	2.3	1.2	-	5.2	8.3	6.9	-	20.8	26.7	23.7	46.16
CaO	69.3	72.4	70.6	73.69	62.2	66.4	63.8	65.12	51.5	58.3	54.6	62.26	47.4	49.9	49.1	
MgO	0.5	2.1	1.1	-	0.2	0.8	0.5	-	0.8	1.5	1.1	-	1.9	3.2	2.6	
K <sub>2</sub> O	<0.1	0.3	0.1	-	0.3	1.9	0.	-	0.3	4.6	2.0	-	0.1	0.3	0.2	
Na <sub>2</sub> O	<0.1	0.3	0.1	-	0.1	0.8	0.3	-	0.2	0.8	0.8	-	0.1	0.2	0.1	

**1.3 Polymorphic Modifications of the Clinker Minerals**

If the clinker minerals are studied in detail, we find out that not only does the chemical composition vary, but the same clinker phase also exists in different polymorphic forms, which can exhibit different physical properties. Determining the various polymorphic forms present in clinker has not been an easy task so that it was first necessary to study the polymorphism of the pure phases C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF in order to obtain sufficient information and experience to be able to advance to alite, belite, aluminate and ferrite.

**1.3.1 C<sub>3</sub>S and Alite**

Between room temperature and 1100 °C **pure C<sub>3</sub>S** displays 6 polymorphic modifications, namely:

- ◆ 3 triclinic T<sub>I</sub>, T<sub>II</sub>, T<sub>III</sub>
- ◆ 2 monoclinic M<sub>I</sub> and M<sub>II</sub>
- ◆ 1 rhombohedral R<sub>I</sub>

From DTA analysis it is known that the transitions take place as follows:



and because the changes involve only a light displacement within the lattice structure (i.e. no breakage of the strong chemical bonds), they are therefore easily reversible. These transformations consequently cannot be prevented, so that in pure C<sub>3</sub>S, the high temperature modifications can only be stabilized by quenching.

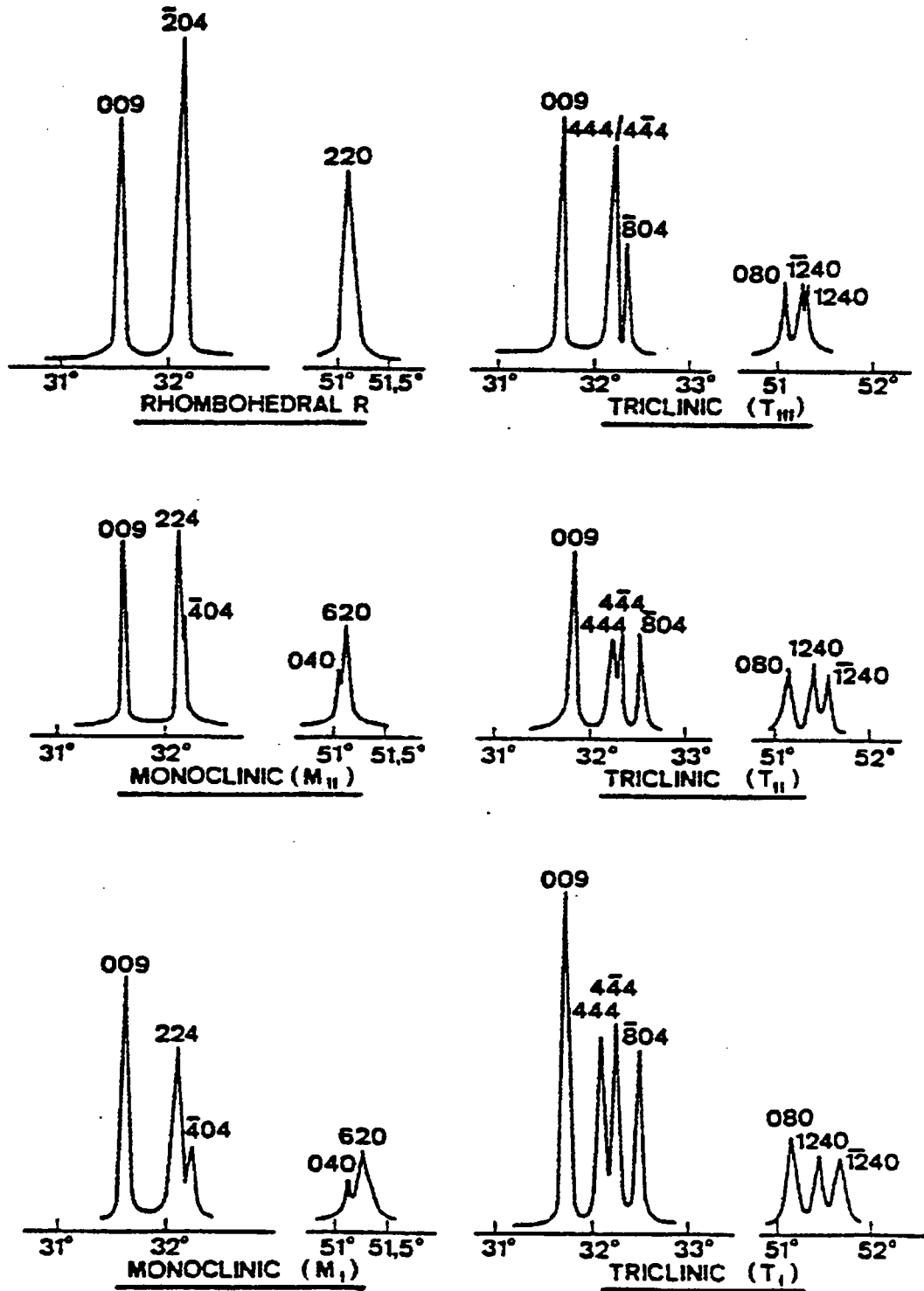
When passing to **alite**, the real mineral in industrial clinker, incorporating Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O, Na<sub>2</sub>O, and TiO<sub>2</sub> within the crystal lattice, it has been found to exist in the following modifications:

- ◆ trigonal R
- ◆ monoclinic M<sub>I</sub>
- ◆ triclinic T<sub>II</sub>

The incorporation of foreign atoms thus ensures the stabilization of the high temperature monoclinic and trigonal forms, and in some clinker even both of these modifications can be simultaneously present. Because the various modifications are crystallographically all very similar, the various polymorphic forms of alite in cement clinker are considered as having essentially the same hydraulic activity. Observed differences in activity seem to be related to structural faults in the crystal as a result of incorporation of elements such as Al, Fe, Mg, etc.

A differentiation between the various polymorphic forms is partially possible by both microscopy and by x-ray diffraction as shown in Figure 5 using sophisticated apparatus and analyzing equipment.

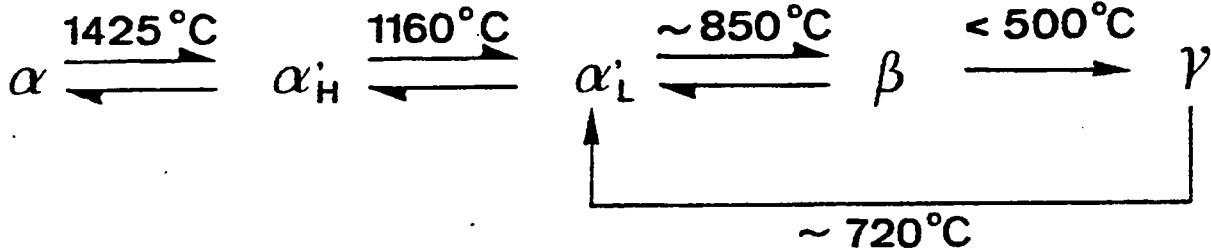
**Figure 5 X-ray diffraction patterns of the various C<sub>3</sub>S polymorphs**



1.3.2 C<sub>2</sub>S and Belite

Pure C<sub>2</sub>S exhibits 5 crystalline modifications between room temperature and 1500°C, namely the form α, β, α<sub>L</sub>, α<sub>H</sub> and α. The stability range of these is displayed in a simplified form in Figure 6.

**Figure 6** Stability ranges and polymorphic sequences of C<sub>2</sub>S

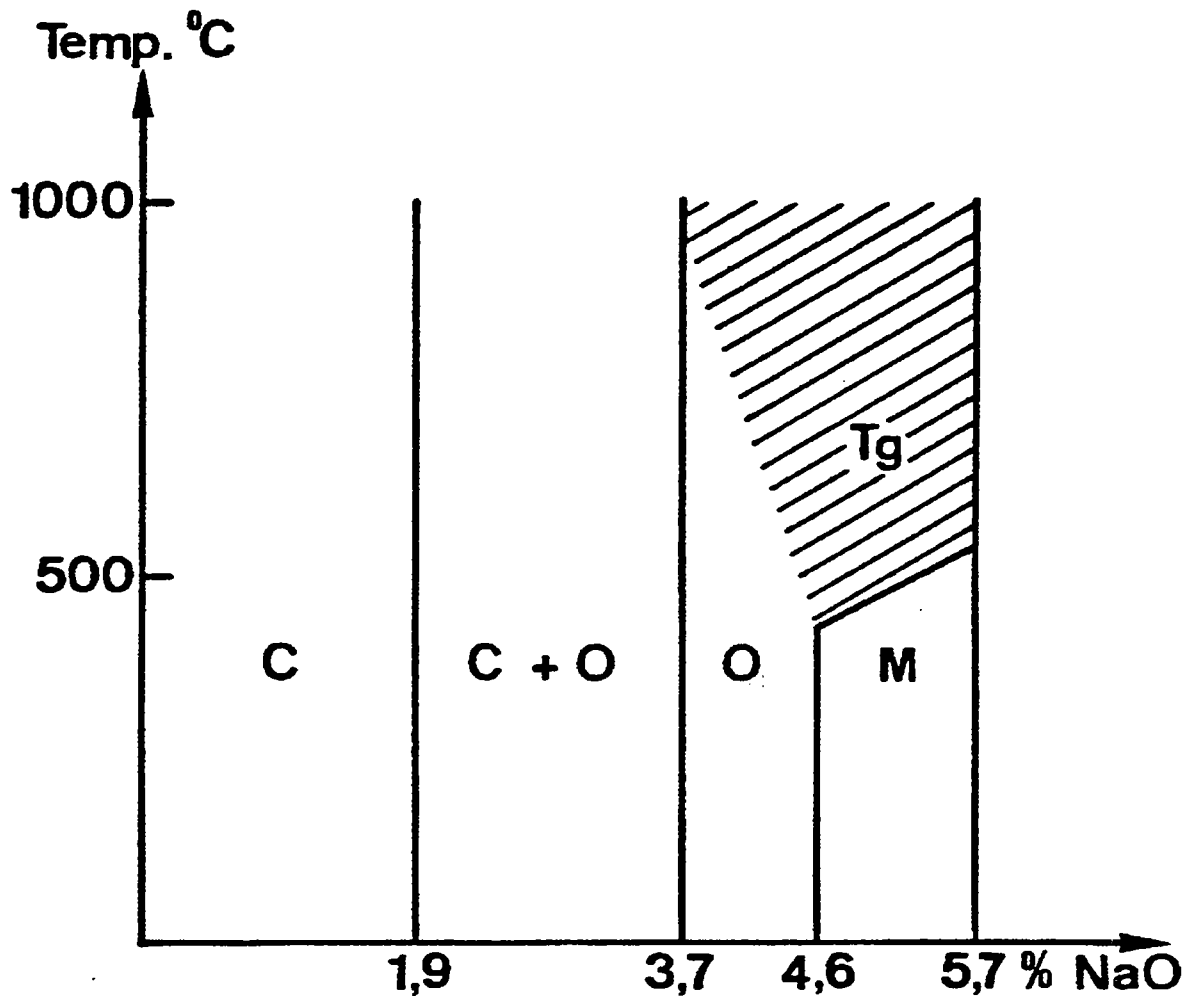


The changes β → α and α → α<sub>L</sub> are irreversible and slow as they involve breaking all the primary chemical bonds. These structural changes are accompanied by a considerable volume change (13 %). The β-belite is considered to have good hydraulicity, while the α-form is hydraulically only little active. Alkalis play an important role: in the presence of K<sub>2</sub>O and Na<sub>2</sub>O and α' and an α-form develop, which have a higher activity than the β-form.

1.3.3 C<sub>3</sub>A and Aluminate

**Pure C<sub>3</sub>A** is a definite compound with a cubic lattice, showing no polymorphic transformations. When increasing quantities of Na<sub>2</sub>O, they are incorporated within the lattice, forming a solid solution series incorporating up to 5.7 % Na<sub>2</sub>O, orthorhombic (O), monoclinic (M) and tetragonal (Tg) modifications occur; their stability relations are summarized in Figure 7.

Figure 7 Phase equilibrium diagram for Na<sub>2</sub>O - C<sub>3</sub>A solid solutions



The **aluminate** phase in clinker exists in the cubic (C), orthorhombic (O) and tetragonal (Tg) forms. Two forms, e.g. O + C or O + Tg, can coexist. Up to date, the monoclinic (M) formation has not been observed. There is some evidence to suggest that the various forms differ in their reactivities.

#### 1.3.4 C<sub>4</sub>AF and Ferrite

**Pure C<sub>4</sub>AF** is not a definite compound but a member of the continuous solid solution series extending between 2 CaO · Fe<sub>2</sub>O<sub>3</sub> and 2 CaO · Al<sub>2</sub>O<sub>3</sub>, the latter end-member being stable only at high pressure, up to approx. 66 % Fe<sub>2</sub>O<sub>3</sub> in 2CaO · Fe<sub>2</sub>O<sub>3</sub> can be replaced by Al<sub>2</sub>O<sub>3</sub>. The member of 4 CaO · Al<sub>2</sub>O<sub>3</sub> · Fe<sub>2</sub>O<sub>3</sub> (C<sub>4</sub>AF) corresponds to the 50 % replacement.

The **ferrite** phase in Portland cement varies chemically between C<sub>6</sub>A<sub>2</sub>F and C<sub>6</sub>AF<sub>2</sub> (solid solution series) and is orthorhombic like the pure C<sub>2</sub>F. As yet no other modification has been reported. The ferrite phase is considered to be only slightly hydraulically active.

For a detailed x-ray diffraction investigation of aluminate and ferrite in clinker, the phases can be concentrated dissolution of alite and belite using salicylic acid.

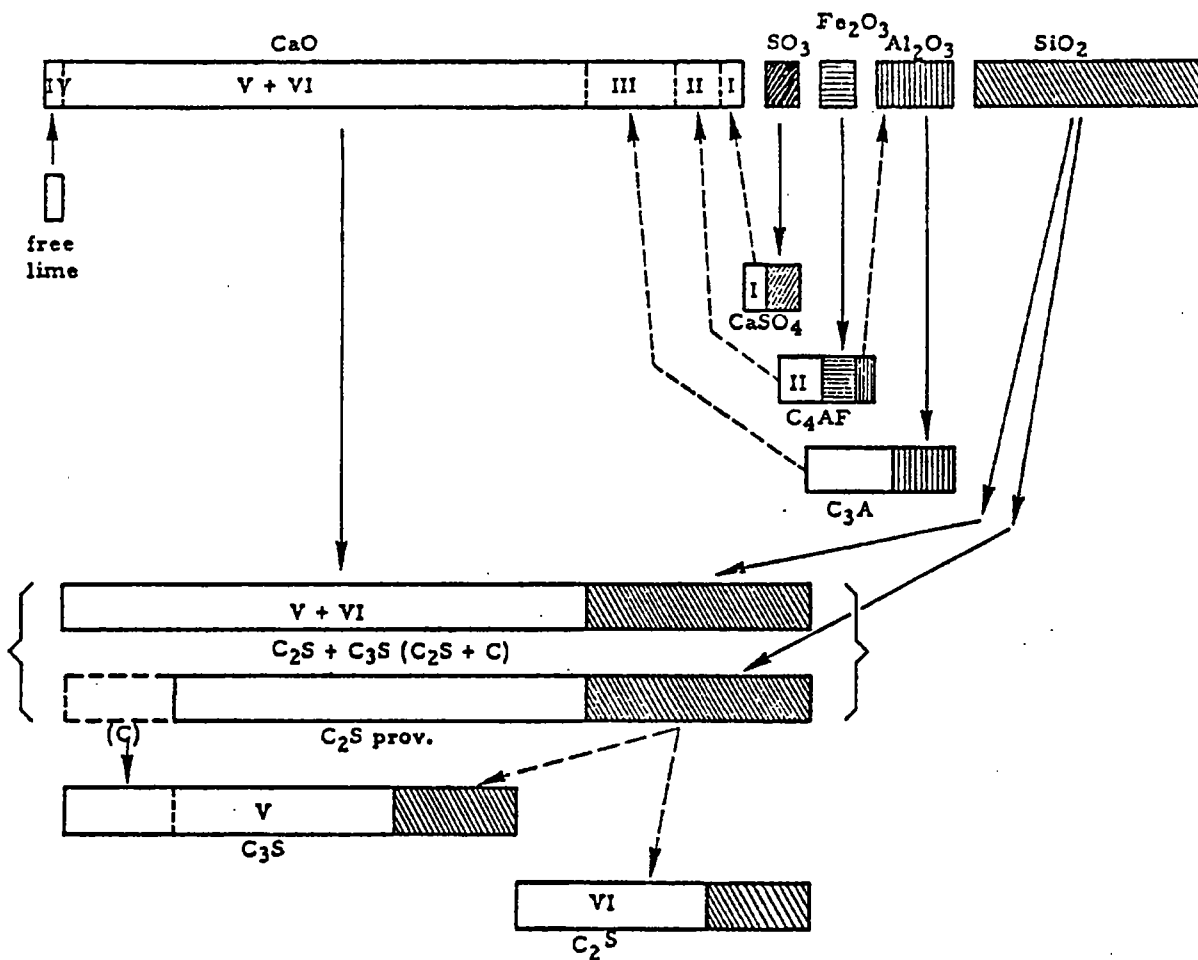
1.4 Quantitative Clinker Mineralogy - Potential and Reality

1.4.1 Calculation of Potential Clinker Composition

For almost 50 years the **potential** clinker mineralogy has been calculated by the procedure first proposed by Bogue. This method assumes that:

- chemical equilibrium has been attained
- $Fe_2O_3$  reacts with  $Al_2O_3$  and  $CaO$  to form  $C_4AF$
- $Al_2O_3$  remaining from combination as  $C_4AF$  reacts with  $CaO$  to form  $C_3A$
- $SO_3$  combines with  $CaO$  to formation  $CaSO_4$
- $CaO$  remaining from the above combinations reacts with the silica.  $C_3S$  is the first formed with the  $SiO_2$ , and any  $CaO$  left over reacts with the  $C_2S$  to form  $C_3S$ . If  $CaO$  remains after converting all of the  $C_2S$  to  $C_3S$  it remains as uncombined  $CaO$ .
- $MgO$  remains essentially uncombined.

Figure 7A Mineralogical composition derived from chemical analysis (Graphical representation of the steps in calculation)



For the purposes of calculation, the 'CaO' and 'SiO<sub>2</sub>' values used are given as

'CaO' =  $CaO_{total} - CaO_{free}$

'SiO<sub>2</sub>' =  $SiO_{2\ total} - insoluble\ residue$

**The calculation does not take into account the influence of the minor elements: alkalis, Mg, Ti, Mn, Cr, P, etc., and the solid solution of the principal oxides: CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> within the alite, belite, aluminite and ferrite phases. As we have already seen, the composition of the 4 principal phases is not C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF. It is therefore not surprising that the potential and real clinker compositions never agree.** This situation is further aggravated by the non-attainment of equilibrium during clinker production. In addition it is now known that SO<sub>3</sub> in clinker is mainly combined with the alkalis and only to a slight extent with CaO. The currently used Bogue formula for clinker does, therefore, not consider the influence of SO<sub>3</sub>.

#### 1.4.2 Differences between Potential and Real Phase Composition

The most practiced method at present to determine the **real** mineralogical composition is by means of microscopic point counting, complemented by the use of crystallized aluminite and ferrite. The results obtained by these methods, as is to be expected, differ from those obtained during the Bogue calculation procedure.

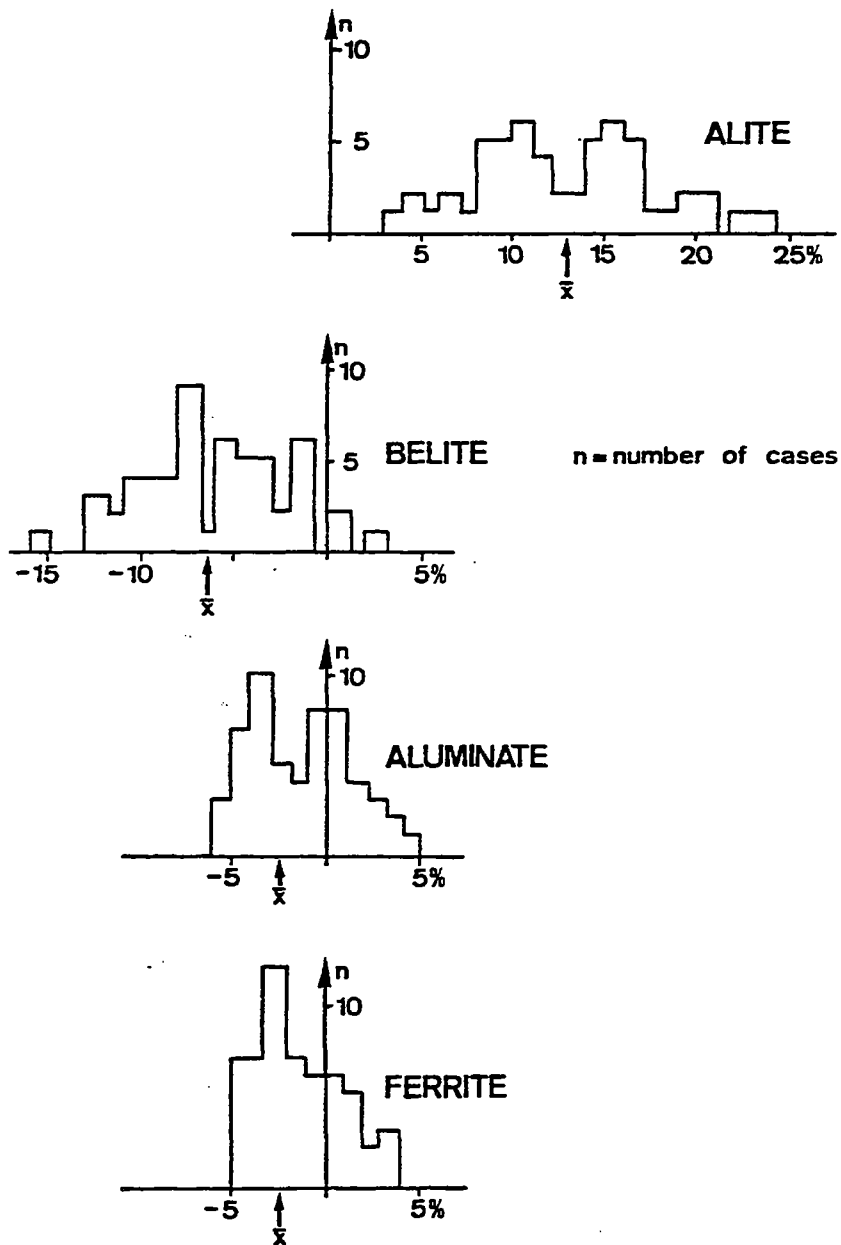
How large are the differences between the potential and real mineralogical composition of the clinker?

This can best be seen in Figure 8 based on the results of measurements on over 50 different plant clinkers (3).

It can be seen that:

- **Alites** as calculated are always **too low**, ranging from 3 - 24 %, on average 13 %
- **Belites** are mostly calculated **too high**, on average 6 %
- **Aluminate and ferrite** as calculated can either be too high or too low, but in general both phases are calculated approx. 2 % too high.

**Figure 8**      **Difference between Actual and Potential Phase Composition**  
**(experimental minus Bogue)**





**1.4.3 Modifications of Bogue's Formula**

A useful improvement in the correlation between potential and real mineralogical composition can be obtained if slight corrections are made to the Bogue calculated values. On the basis of data obtained (Figure 8), the following formulae have been proposed:

$C_3S_{corr.}$	=	$C_3S_{Bogue} + 4.0 MgO_{clinker} + 5.5 K_2O_{clinker}$
$C_2S_{corr.}$	=	$C_2S_{Bogue} - 1.5 MgO_{clinker} - 2.2 K_2O_{clinker}$
$C_3A_{corr.}$	=	$C_3A_{Bogue} + 7.8 Na_2O + 1.5 AR - 2.1 SO_3 - 5$
$C_4AF_{corr.}$	=	$C_4AF_{Bog} - 6.5 Na_2O - 1.7 AR + 5.0 Mn_2O_3 + 3$

These corrected formulae are valid under the following conditions:

$MgO < 4 \%$	$Na_2O < 0.5 \%$	$Mn_2O_3 < 0.3 \%$
$K_2O < 1 \%$	$SO_3 < 1.0 \%$	$AR > 1.0$

In the case of  $AR < 1.0$  uncorrected Bogue's formulae are more precise to calculate  $C_3A$  and  $C_4AF$ .

The improvement achieved by using these modified formulae can be seen in Figures 9 and 10. These corrections improve Bogue's original concept in that the clinker phases can be more accurately calculated, taking into consideration the incorporation of minor elements without having to undertake time consuming mineralogical analyses.

For pure routine quality control purposes in any individual plant, the use of the original Bogue equations is still acceptable as long as no significant change in raw materials occurs. For comparison of calculated values between different plants or with directly measured clinker mineralogy (microscopy, x-ray diffraction) the use of the modified formulae is recommended.

Figure 9 Alite and Belite

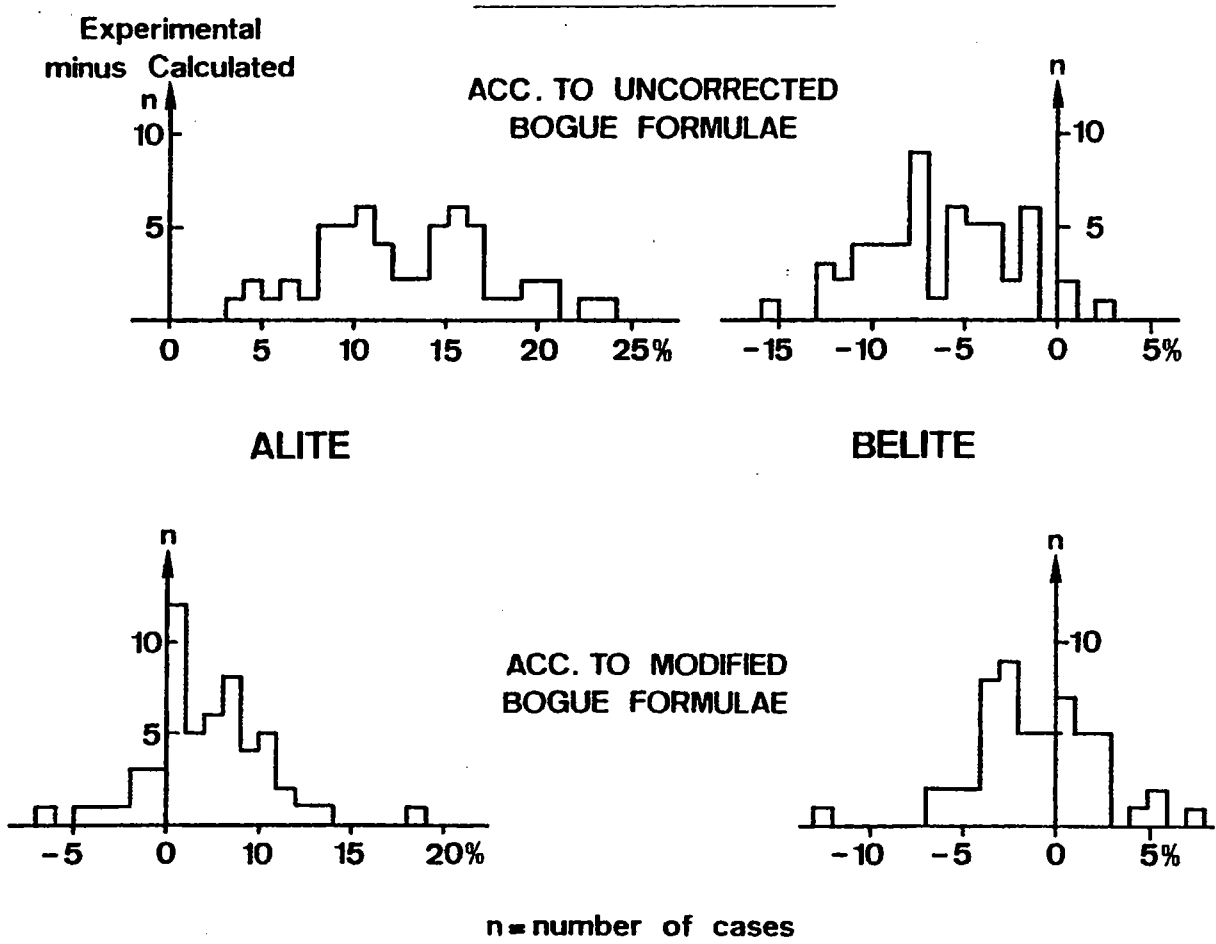
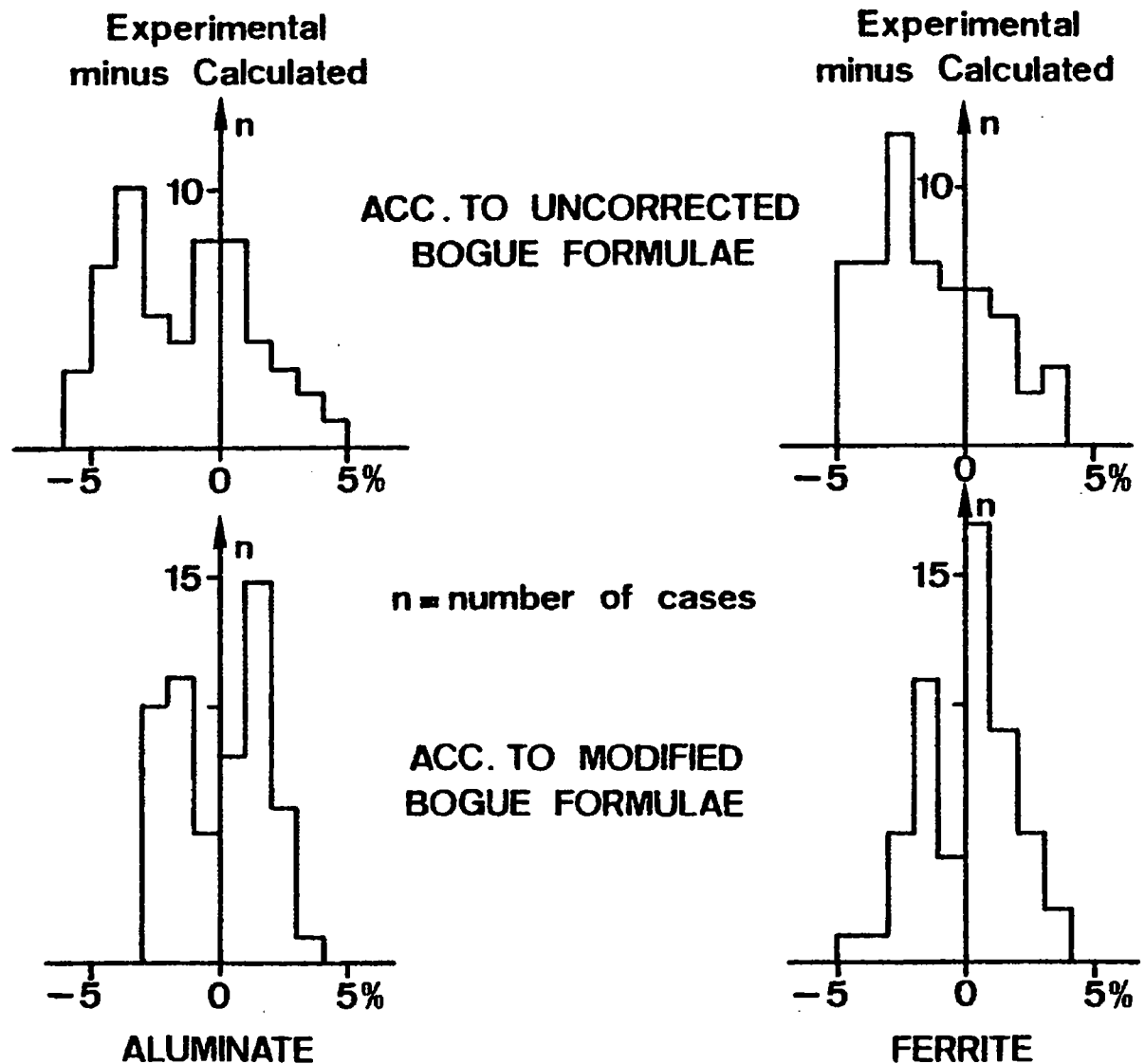


Figure 10 Aluminate and Ferrite



## 2. CLINKER MICROSTRUCTURE

### 2.1 Microscopical Appearance of the clinker minerals

#### 2.1.1 Introduction

In the foregoing chapter we have discussed the principles of clinker formation, its chemistry and mineralogy. These parameters can only account for part of the clinker and of the resulting cement properties. The microstructure or fabric of a clinker is also decisive when considering phenomena such as clinker grinding, cement hydration and hardening characteristics.

In this chapter only an introduction to the microscopical appearance of industrial clinker will be given. As this is a complex topic, only the basic principles will be discussed. For further information reference should be made to any of the reference works on this subject (4, 5).

### 2.1.2 General

The appearance of a crystalline aggregate is generally referred to as fabric, which is defined as the whole of all geometric features or properties of an aggregate. Three groups of geometric features can be discerned: **phase association, texture and structure.**

**Phase association** is the information group which defines what phases constitute the fabric and in what quantities they exist. **Texture** includes the information concerning size, shape and arrangement of the crystals and also the intergrowth relationship of the individual phases. Finally, **structure** indicates to what extent a fabric is anisotropic, whether some crystal phases are oriented in a certain direction and what type of space-filling, i.e. porosity, occurs.

With these geometric features, we can describe the fabric of a material. This description explains **how** and out of **what** a piece of clinker is build up. When completely differently manufactured clinkers are investigated and compared, one realizes to what degree the ‘what’ and ‘how’ differ, thereby resulting in the most varied clinker fabrics.

The fact that clinker does not always have the same appearance leads to the important question of why one particular fabric and not another is formed. It is overall accepted that the genesis of a crystalline material influences to a great extent its appearance or fabric. The genetic factors of the clinker formation process are identical to those conditions on which the industrial manufacture of clinker is based, this being the interaction of parameters beginning with the raw material, passing through the sintering process and ending with clinker storage.

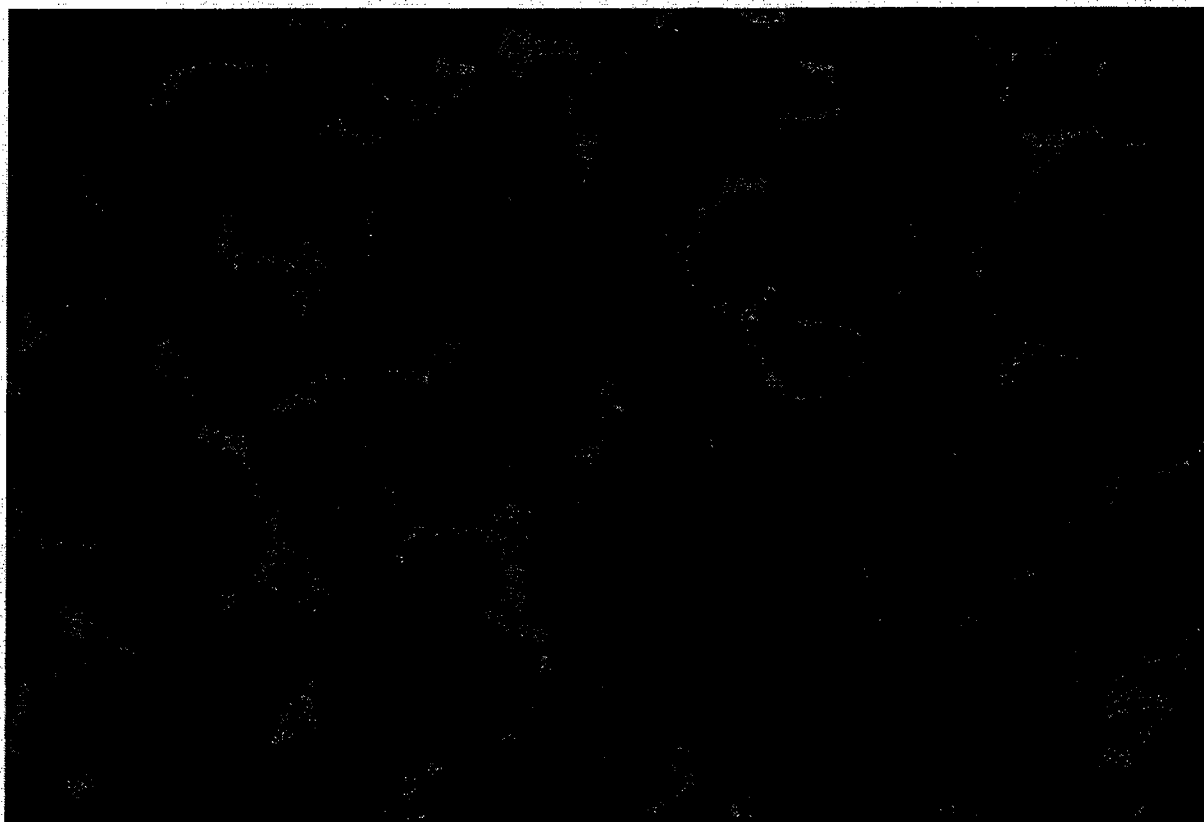
### 2.1.3 Microscopical Appearance of Clinker Phases

#### 2.1.3.1 *Alite*

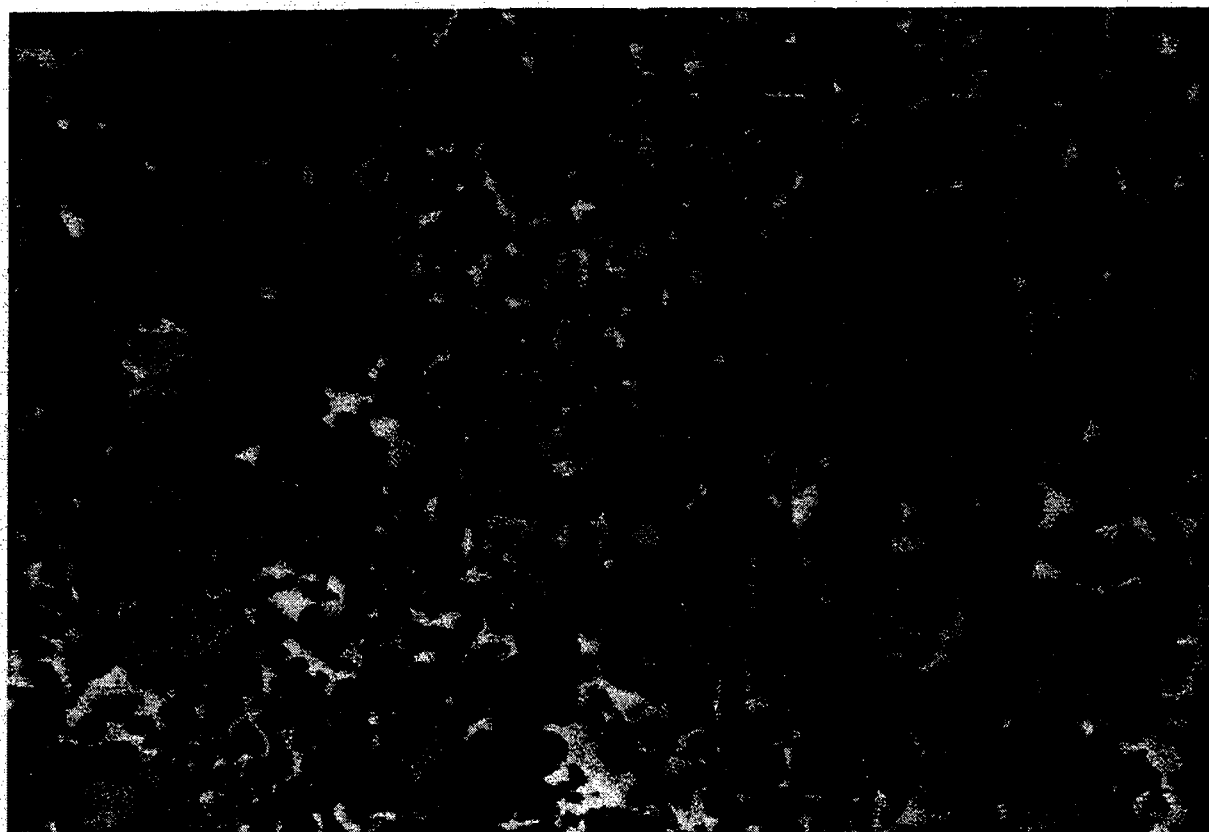
##### **External Form**

Alite, the principal constituent of cement clinker, occurs most frequently as idiomorphic crystals, i.e. as well-defined, sharp-edged crystals. The characteristic form, as can be seen in Plate 1, are compact tabular crystals, often exhibiting a hexagonal section. Alite crystals can also, however, be found in a form whose outlines are dissected by indentations and protrusions, and whose hexagonal shape is barely discernible. Such crystals are termed xenomorphic alite and can be seen in Plate 2. Lath-shaped alite crystals have also been reported.

**Plate 1**      **Idiomorphic alite (brown). 250 x**



**Plate 2**      **Xenomorphous alite. 250 x**



### Internal Features

A feature commonly observed within alite crystals is the inclusion of small rounded belite crystals, these having been formed before the alite, as has previously been indicated in Paper 10. An example of this phenomenon can be seen in Plate 3.

#### **Plate 3 Alite exhibiting belite (blue) inclusions. 250 x**

Other features can also be observed within alite crystals and include the presence of single and polysynthetic twinning, as can be seen in the excellent plates in Ref. 4 (p. 11, Fig. 4).

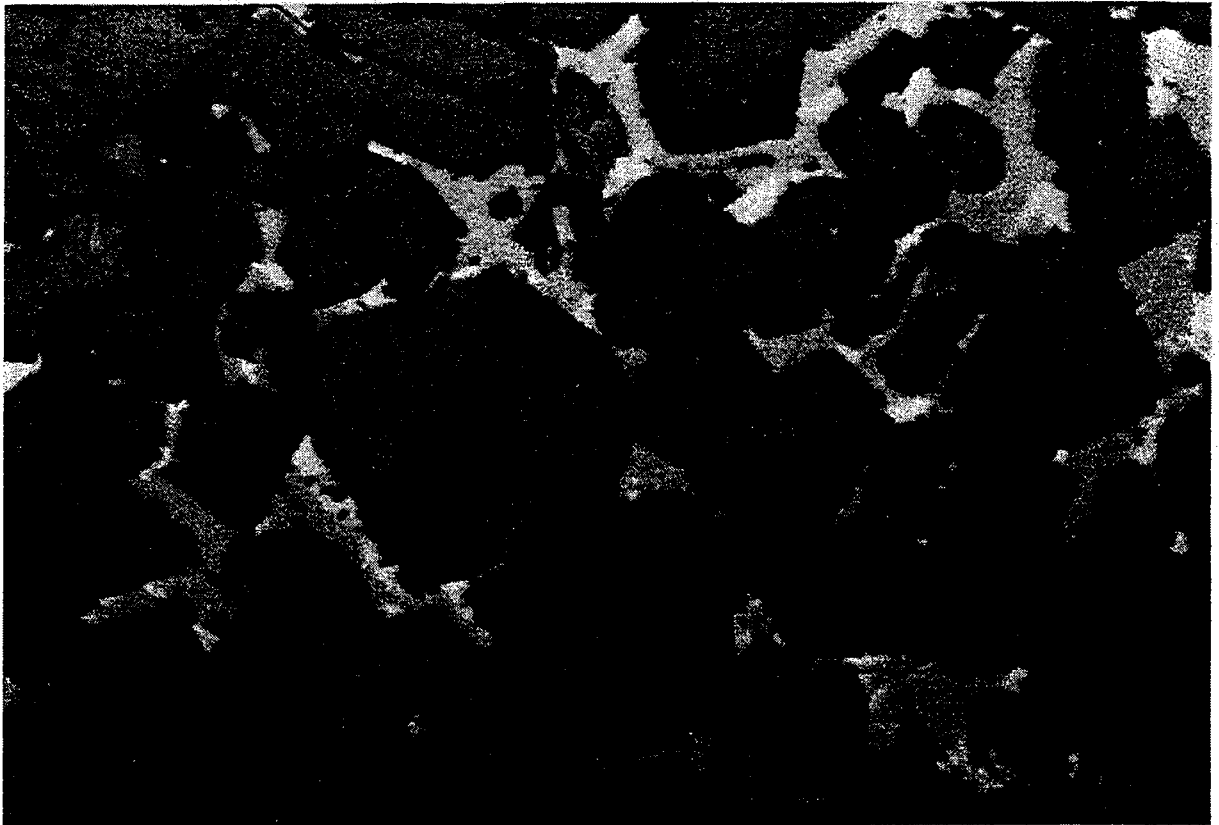
At the highest sintering temperature, alite always exhibits its highest symmetry, i.e. trigonal (R) form, but on cooling to normal temperature, passes through several polymorphic stages, and so in industrial clinker appears mostly in the monoclinic (M) and triclinic (T) forms. **The presence of simple twinning is indicative of crystals having passed through the trigonal (R) → monoclinic (M) polymorphic transition. The presence of polysynthetic twinning is associated with the change from the monoclinic to the lowest symmetry, i.e. triclinic (T) form.** Differentiation between the individual monoclinic or triclinic forms is not possible by microscopy but requires the use of x-ray diffraction (see Figure 5) or DTA techniques. The optical distinction of the various polymorphic changes is made possible by the different etching behavior of the various crystal modifications.

Another internal feature of alite crystals is the presence of zones having different etching properties, i.e. a zonal structure. These zones are associated with the selective inclusion of different ions during the formation process. Examples of the various forms of twinning and zonal structure are to be found in (4).

### **Alite decomposition**

As has already been mentioned, pure  $C_3S$  is unstable below 1250 °C and tends to decompose into belite and sub-microscopic free lime. Although **this decomposition is strongly suppressed in alite due to the incorporation of foreign ions**, the presence of bivalent iron i.e.  $Fe^{2+}$  and  $CaF_2$  opposes this stabilization effect. An example of partially decomposed alite crystals can be seen in Plate 4.

**Plate 4      Alite decomposition into belite and free lime. 250x**



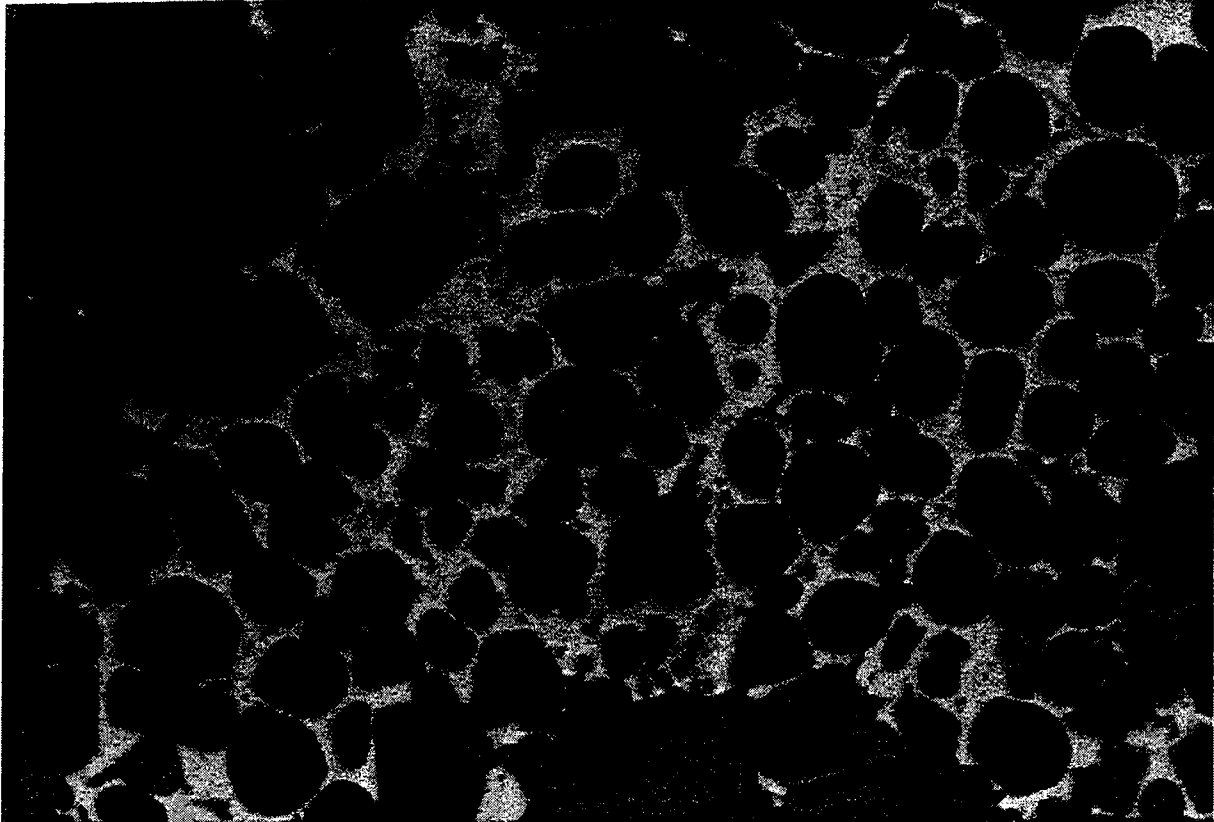
**Scanning electron microscope (SEM) photographs of alite, (see Plates 21 - 23) also indicate the idiomorphic formation shown in Plate 1.**

2.1.3.2 *Belite*

**External Form**

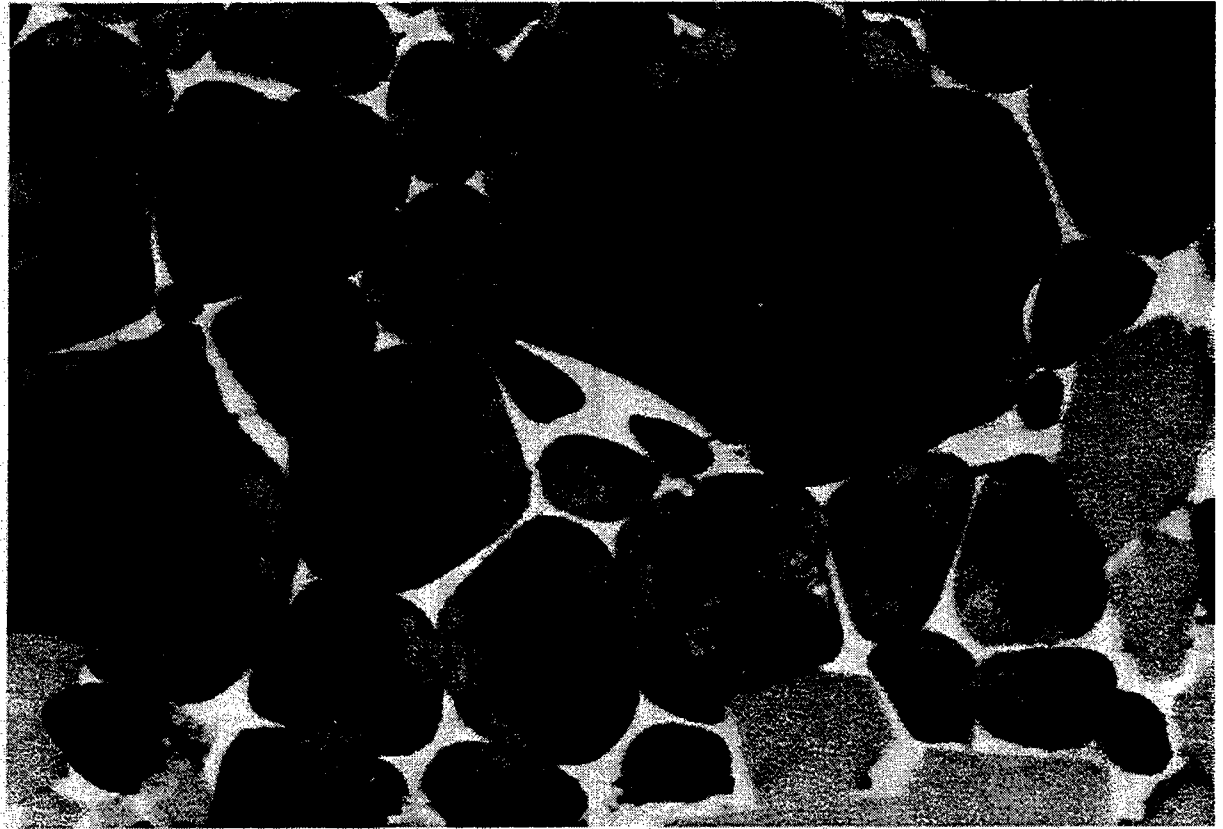
The round crystal form (Plate 5) is the most characteristic shape of belite, although in rare cases crystals showing a tendency to a hexagonal form are also observed (Plate 6).

**Plate 5**      **Typical rounded belite 250x**





**Plate 6      Belite with complex lamellar structure due to  $\alpha \rightarrow \alpha'$  transition. 640x**



### Internal Features

Just like in the case of alite, the passing through the  $\alpha \rightarrow \alpha'$ ,  $\alpha' \rightarrow \beta$  and  $\beta \rightarrow \alpha$  polymorphic transformations can also be microscopically observed. The first mentioned transition realities in belite crystals exhibiting a **cross lamella structure** as shown in Plate 6, while after undergoing the  $\alpha \rightarrow \beta$  transition, **polysynthetic twinning** occurs.

Cross lamella and polysynthetic twinning can sometimes be observed in the same crystal.

The transition from  $\beta \rightarrow \alpha$  belt, accompanied by an appreciable change of volume can be observed microscopically.

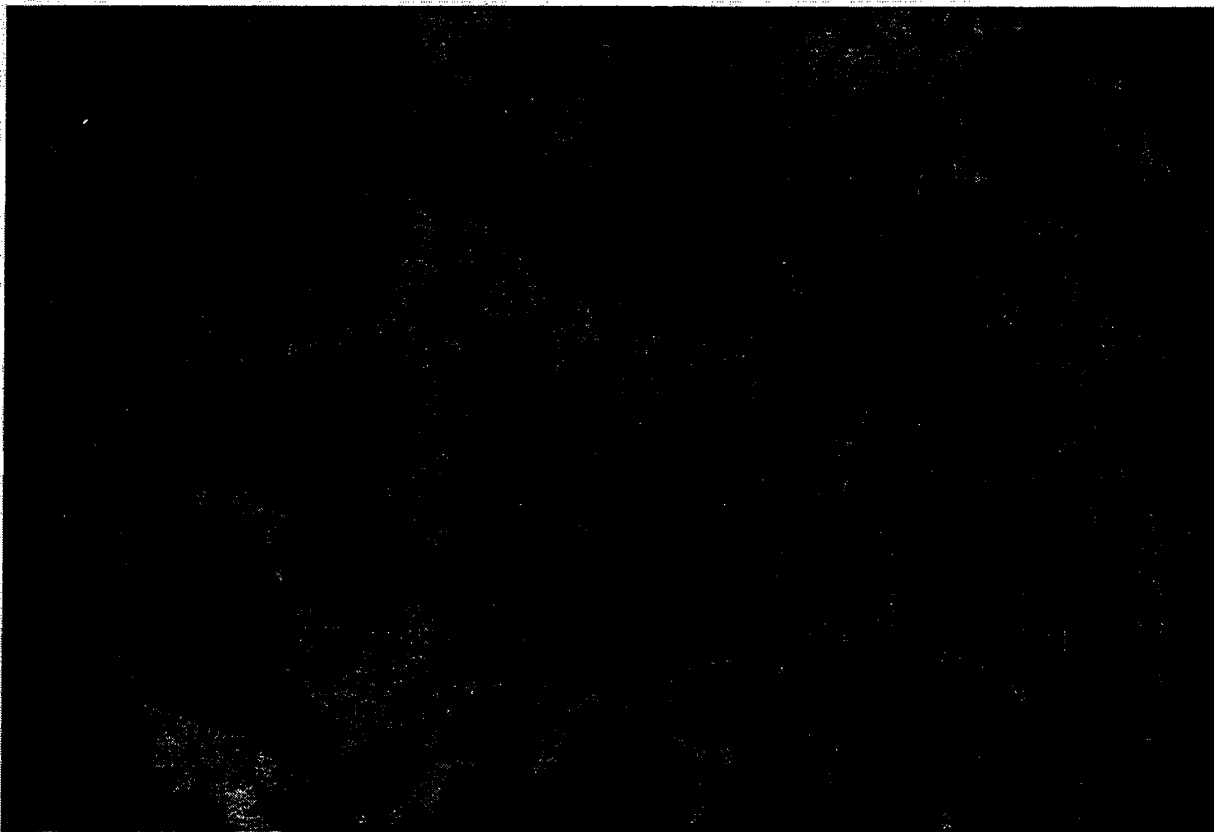
$\alpha$  - belite is undesirable in clinker because the strong volume expansion breaks up the clinker granules, producing much dust, and also because it is not hydraulically active.

Excellent plates showing polymorphic transformation phenomena are to be found in (4).

### Secondary Belite

The liquid in contact with alite and belite at clinking temperature contains approximately 6 %  $\text{SiO}_2$  as well as  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . During cooling, immediately after the maximum temperature, this  $\text{SiO}_2$  comes out of solution in the form of small secondary belite crystals as shown in Plate 7. Such belite can exhibit a drop-like or dendritic structure.

**Plate 7      Secondary crystallization of belite 250 x**



Scanning electron microscope photographs of belite seen in Plate 22 also confirm the rounded shape of belite observed in polished sections.

*2.1.3.3 Uncombined Lime*

This is more commonly known as **free lime**, and always appears as rounded spherical crystals (Plate 8), even when it is not constricted by other crystalline phases. When viewed at higher magnifications, e.g. 10,000 through scanning electron microscopy as shown in Plate 24, it can be seen that the rounded free lime grains do have planar surfaces. It is invariably found along with alite, but not in contact with belite, as in the latter case the two would react to form alite.

**Plate 8**      **Spherical free lime (off-white) 250 x**



Uncombined lime should not be confused with the micro-crystalline secondary free lime, resulting from the decomposition of alite.

*2.1.3.4 Matrix*

The principal clinker minerals alite and belite are surrounded at clinking temperature by a liquid phase (matrix). Upon cooling the latter crystallizes to yield principally aluminate and ferrite but, depending upon its composition, can also yield periclase and sulfate containing minerals.

*2.1.3.5 Aluminate*

The form of the aluminate phase depends both upon the cooling rate and the alkali content of the liquid phase. When the cooling rate is slow, well-separated idiomorphic aluminate crystals can be observed (and consequently also ferrite crystals), as can be seen in Plate 9. This type of aluminate is the normal or cubic form, containing insufficient incorporated foreign ions (alkalis) to change its symmetry to one of the lower symmetry types.

**Plate 9      Differentiated aluminate (gray) and ferrite (white) caused by slow cooling. 640 x**



When the liquid phase is rich on alkalis, an aluminate solid solution containing both  $K_2O$  and  $Na_2O$  crystallizes in the elongated lath form shown in Plate 10, often termed 'alkali aluminate'.

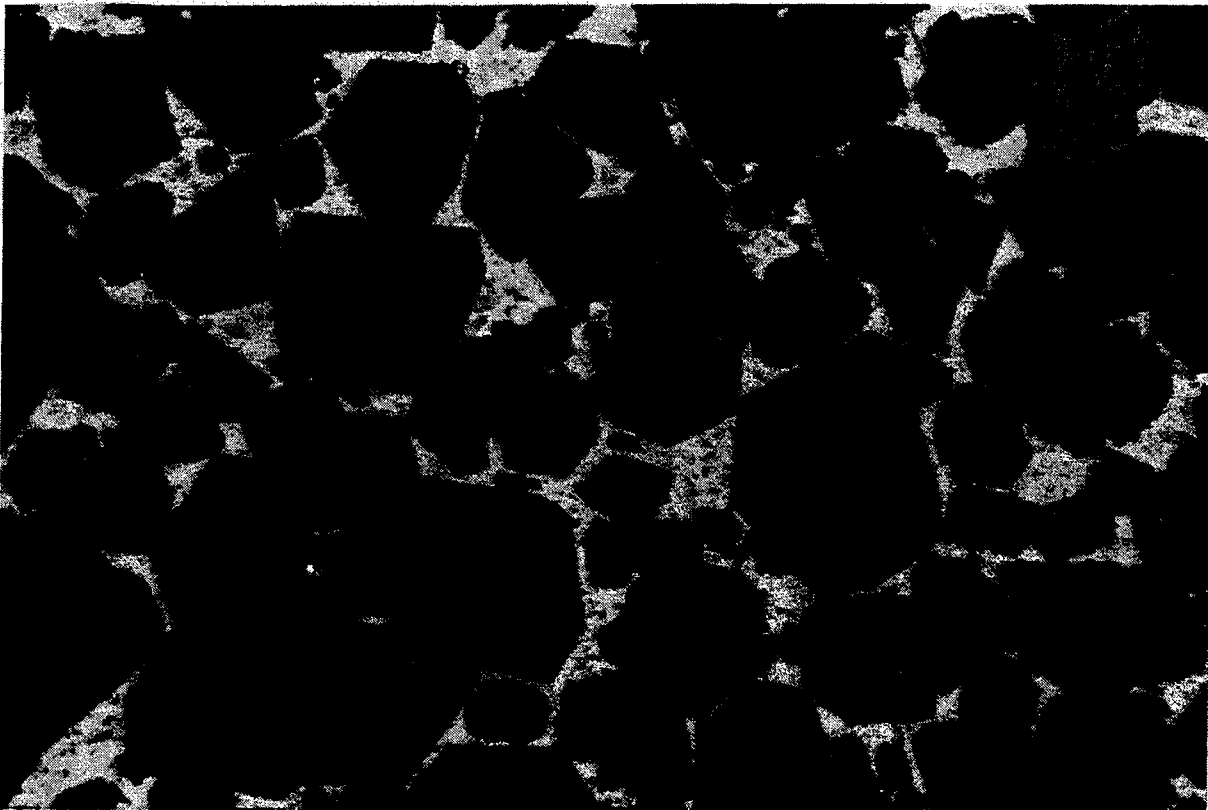
**Plate 10      Alkali aluminate with lamellar habit. 570 x**



This form, as has been reported earlier, may have orthorhombic (O) or tetragonal (Tg) crystal symmetry, requiring x-ray diffraction to differentiate between the two modifications.

However, when the clinker has been rapidly cooled, the aluminate and ferrite are finely grained and closely intergrown as shown in Plate 11.

**Plate 11** Finely grained aluminate and ferrite due to rapid cooling. 250 x



Although the individual crystals are often so fine that they cannot be optically distinguished, x-ray diffraction confirms that they are present in a crystalline and not amorphous form.

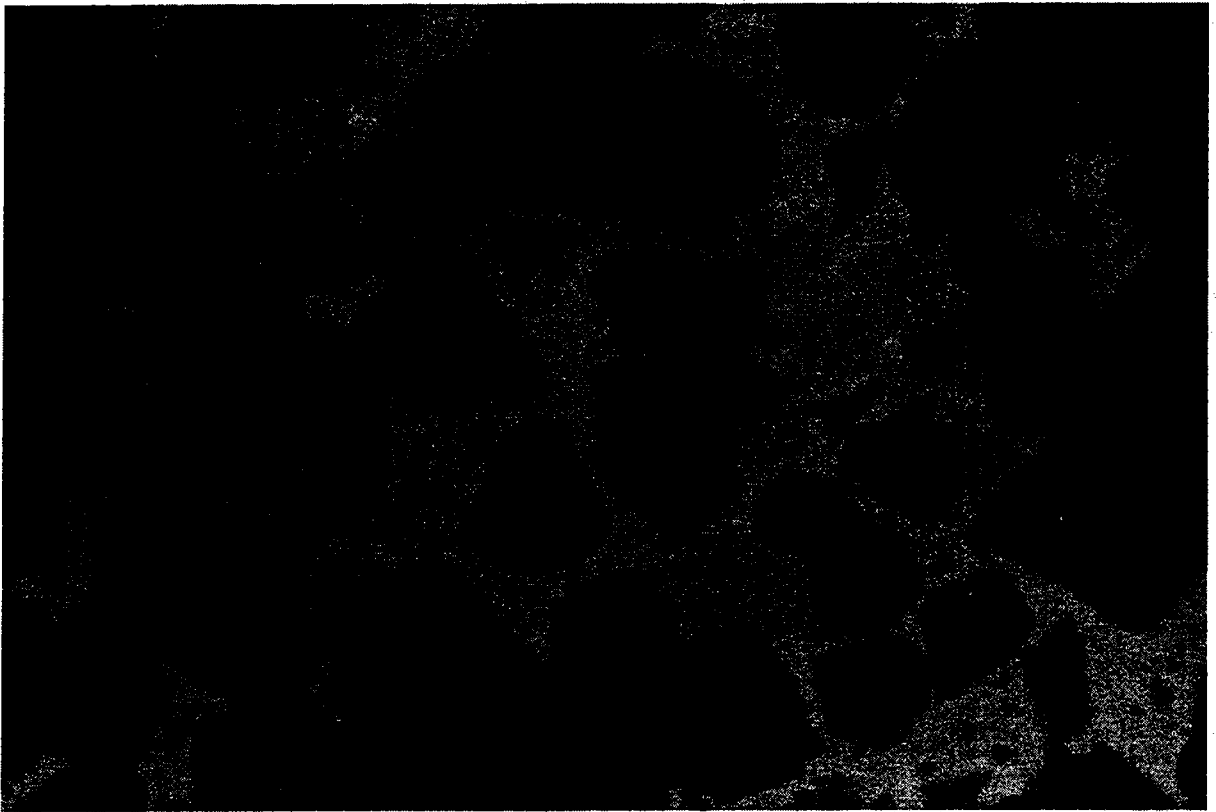
*2.1.3.6 Ferrite*

Just like the aluminate, the external form of the ferrite, as can be seen in Plate 9 and 11, depends upon the cooling rate. The composition of this phase varies, due to solid solution, around the ratio  $C_4AF$ . The actual value cannot be determined by microscopy but x-ray diffraction gives an indication of their composition.

*2.1.3.7 Periclase*

Periclase occurs only in clinker rich in MgO as an independent phase. In general two types can be distinguished, one idiomorphic with polygonal sections, and one dendritic. Periclase is very easily identified under the microscope due to its resistance to grinding and etching.

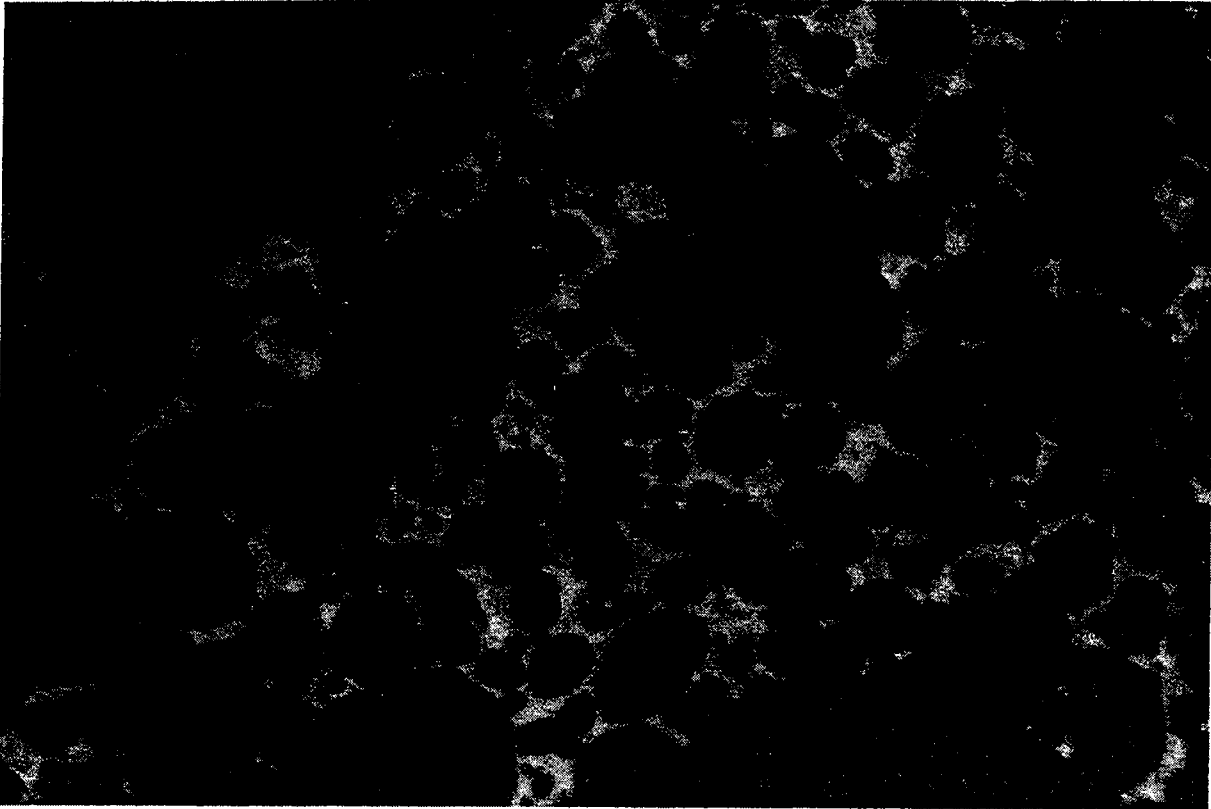
**Plate 12      Idiomorphic periclase (gray). 640 x**



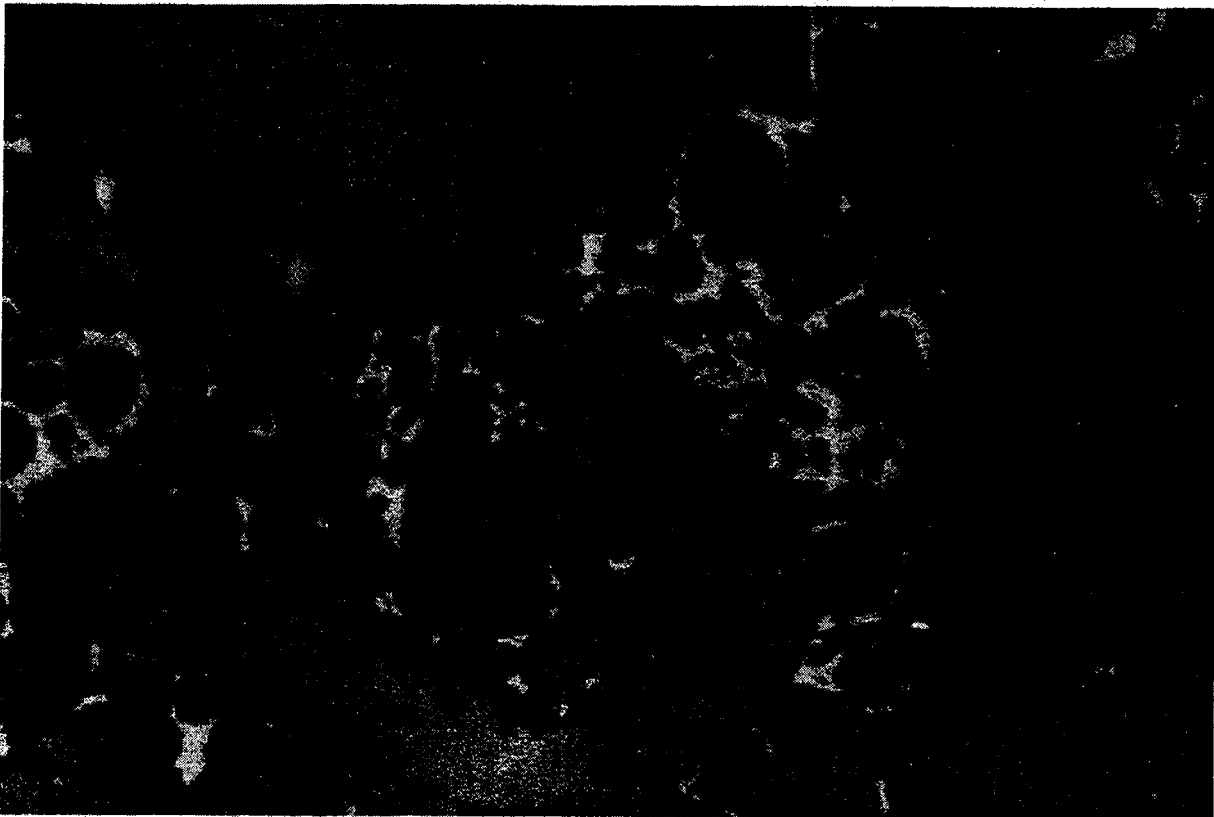
*2.1.3.8 Sulfate containing phases*

The last phases to crystallize, long after the aluminates and ferrites have solidified, are the alkali sulfates. These have been identified as being of two separate types, namely a simple alkali sulfate of composition  $K_2SO_4$ , and a calcium potassium sulfate of composition  $2CaSO_4$ , both being able to incorporate small amounts of sodium. They are often found around the edges of pores. Micrographs showing these two types of sulfates can be seen in Plates 13 and 14.

**Plate 13      Alkali sulfate (black, angular) 250 x**



**Plate 14      Calcium potassium sulfate (needle shaped). 250 x**





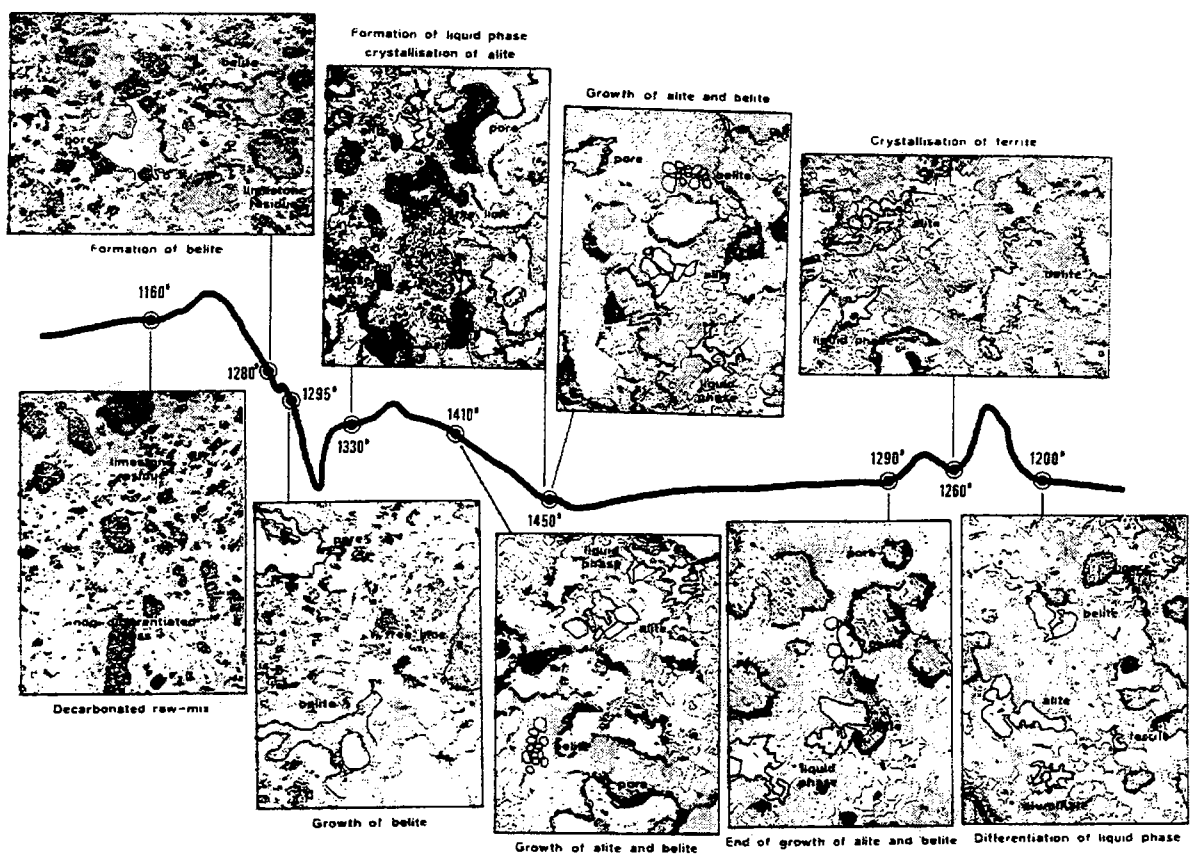
## 2.2 Formation of Clinker Microstructure During Burning

As clinker formation takes place over a range of temperature, it is not surprising that a gradual change of fabric occurs between the initial raw meal and the finally cooled clinker.

The most common way of ascertaining such changes is to microscopically examine polished sections prepared from raw materials which have been heated to selected temperatures and then immediately quenched, to retain their high-temperature microstructure. Suitable samples may be either obtained via sampling parts located at various positions along a kiln shell, or by heating raw mixes in the laboratory. Now following, the change of microstructure of samples obtained at various temperatures during clinkering in a laboratory DTA investigation are summarized.

As can be deduced from Figure 11 and from other sources (6), the clinker on attaining the various indicated temperatures, shows the following changes in microstructure:

**Figure 11 Changes in Microstructure at various temperatures**



### Upheating cycle:

**1160°C**

Individual particles of decarbonized limestone (i.e. free lime) and unreacted hematite can be seen against the sub-microscopic, non-differentiated mass. Quartz particles are surrounded by reaction rims, several microns thick. The presence of free lime and belite can be demonstrated by x-ray diffraction. No large pores can be observed.

**1280°C**

The reaction rim around quartz particles has now become thicker and developed into rounded belite crystals, large enough to be optically identified. The outline of large decarbonized limestone grains can still be recognized. The presence of large pores is now observed.

**1295°C**

Quartz grains have mostly disappeared and in their place are now grains of belite. While new belite crystals are formed, the already existing ones at the same time increase in size. Small pockets of liquid phase can already be observed. The structure is now decidedly porous.

**1330°C**

The presence of liquid phase is very evident at this temperature, as is the presence of optically identifiable alite and free lime crystals.

**1410°C**

Alite and belite crystals are still growing and showing their typical morphological forms in liquid rich zones. Large pores can still be observed.

**1450°C**

Alite and belite have further increased in size but have still not reached their final dimensions. Free lime can still be observed in many areas of the clinker in its typical rounded form.

**Cooling Cycle:****1290°C**

Alite and belite have reached their final size while porosity has generally decreased. The liquid phase is still undifferentiated.

**1260°C**

Crystallization of the ferrite phase from the melt is detectable (see DTA curve).

**1200°C**

The clinker has its final microstructure. Alite and belite can now be observed in a matrix consisting of crystallized aluminate and ferrite of sufficient size so as to allow their identification. Alite often appears to have been resorbed (xenomorphic crystals), while on account of slow cooling belite often shows finger-like growths. Small areas of exsolved material can sometimes be seen within aluminate areas, i.e. secondary crystallization of belite has occurred.

**2.3 Influence of Production Conditions on Clinker Microstructure**

**2.3.1 General**

The microstructure of industrially produced clinker is influenced by several process parameters, the most important of which are given in Table 2.

**Table 2 Industrial parameters influencing clinker texture**

Influence Parameter	Specific factors
Raw mix properties	chemical composition fineness and Mineralogy homogeneity
Fuel type	coal ash
Burning conditions	burning time / temperature kiln atmosphere
Cooling conditions	rate of cooling

**2.3.2 Chemical Composition**

If burning is properly performed, the quantitative mineralogical composition of a clinker depends only on the chemical characteristics of the raw feed. From theoretical considerations (phase diagrams and Bogue calculation) and microscopical observations, the change of clinker mineralogy with varying clinker compositions can be predicted.

Although it may seem trivial, it is considered useful to give the clinker mineralogy associated with clinker chemical composition (Table 3).

**Table 3 Effect of chemical composition on clinker mineralogy**

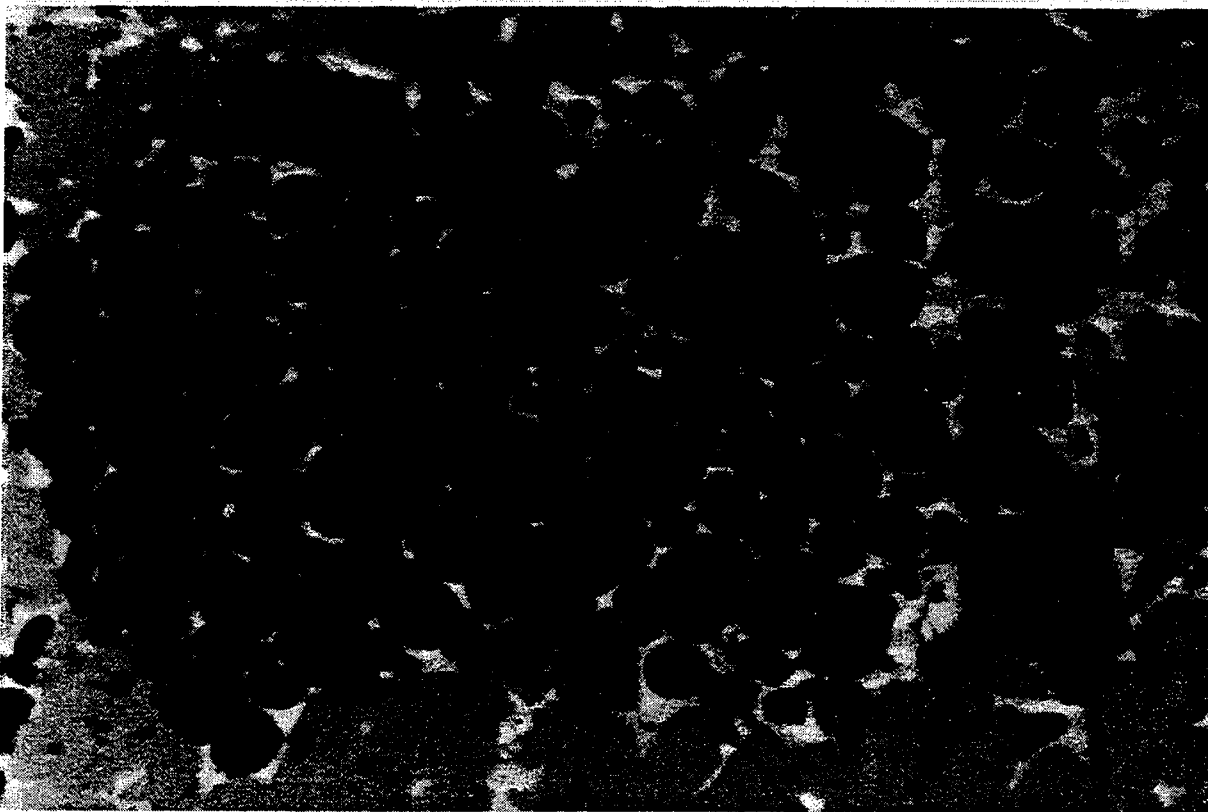
Chemical composition	Clinker mineralogy	
lime saturation too low	alite belite free lime	little abundant traces
lime saturation too high	alite belite free lime	abundant little excessive
alumina ratio high	aluminate > ferrite	
alumina ratio low	ferrite > aluminate	
silica ratio high	little liquid phase	
silica ratio low	liquid phase abundant	
alkalis	alkali - aluminate present	
alkalis together with SO <sub>3</sub>	alkali - sulfates present	
more Mg than can be incorporated in the lattice of principal phases	periclase present	

### 2.3.3 Fineness and Mineralogy

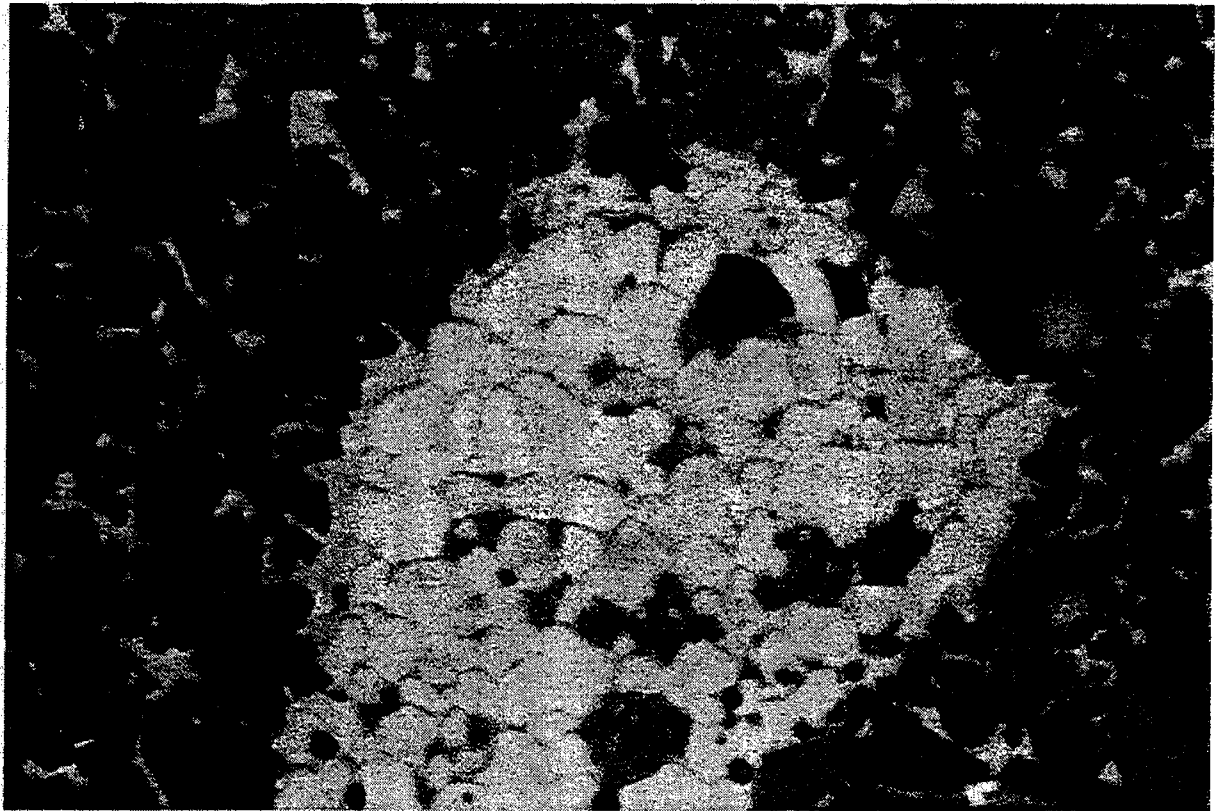
During the clinkering of a raw mix, a migration and exchange of material takes place. The smaller the grain size, the shorter the transport distance required to achieve complete reaction.

Once a certain grain size is exceeded, the lime and quartz components can no longer react completely within the allowed time. Critical particle size for minerals such as calcite and quartz lie in the range of approx. 50 - 100  $\mu\text{m}$ . The maximum grain size is, therefore, that at which the raw material particles are still just able to react. When this limit is exceeded, 'undigested' relicts remain. If the clusters of free lime and belite are examined, particularly those with sharp boundaries (Plates 15 and 16), it is evident that they owe their formation to the presence of oversize raw material grains. They still show the original appearance of a raw meal grain, the siliceous particles being present as belite clusters and the carbonate particles as free lime clusters as a result of incomplete reaction.

**Plate 15**      **Belite cluster due to large,  $\text{SiO}_2$  - rich grain. 220 x**



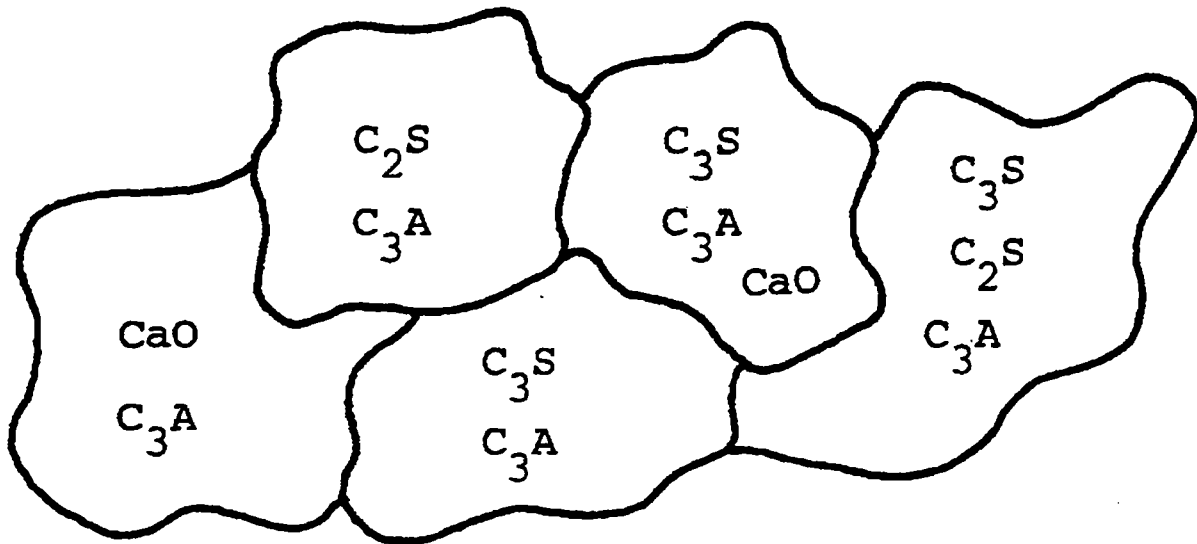
**Plate 16** Free lime cluster due to large, lime-rich grain. 64 x



2.3.4 Homogeneity

If the raw mix is insufficiently homogenous, volume units of varying size will exist which do not have the overall bulk chemical composition. It is easy to deduce from the phase diagram for the system  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{SiO}_2$  the phase compositions which can coexist assuming different volumes to have different chemical composition. In Figure 12 the different phase assemblages in the system  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  can be seen.

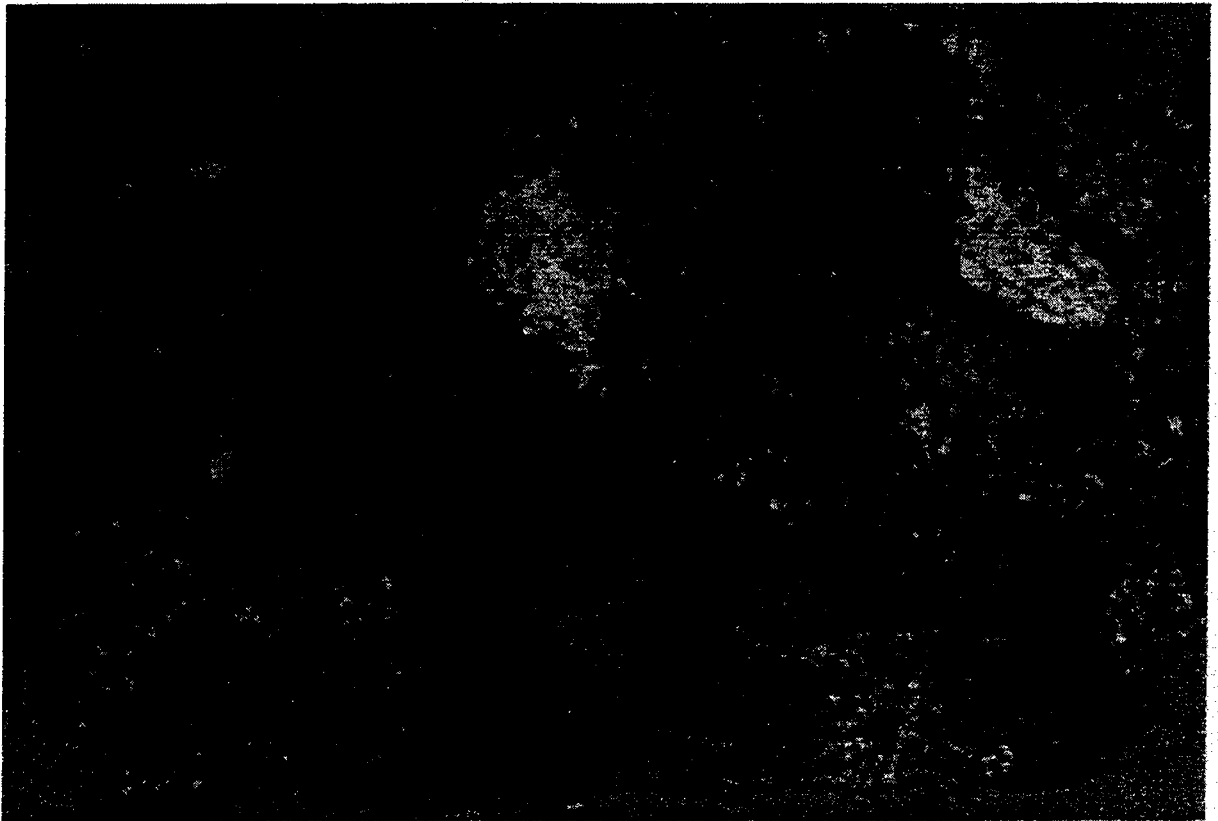
**Figure 12** Possible mineral assemblages in the system  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$



With insufficiently homogenous raw feeds we should therefore expect a clinker microstructure of varying mineralogy.

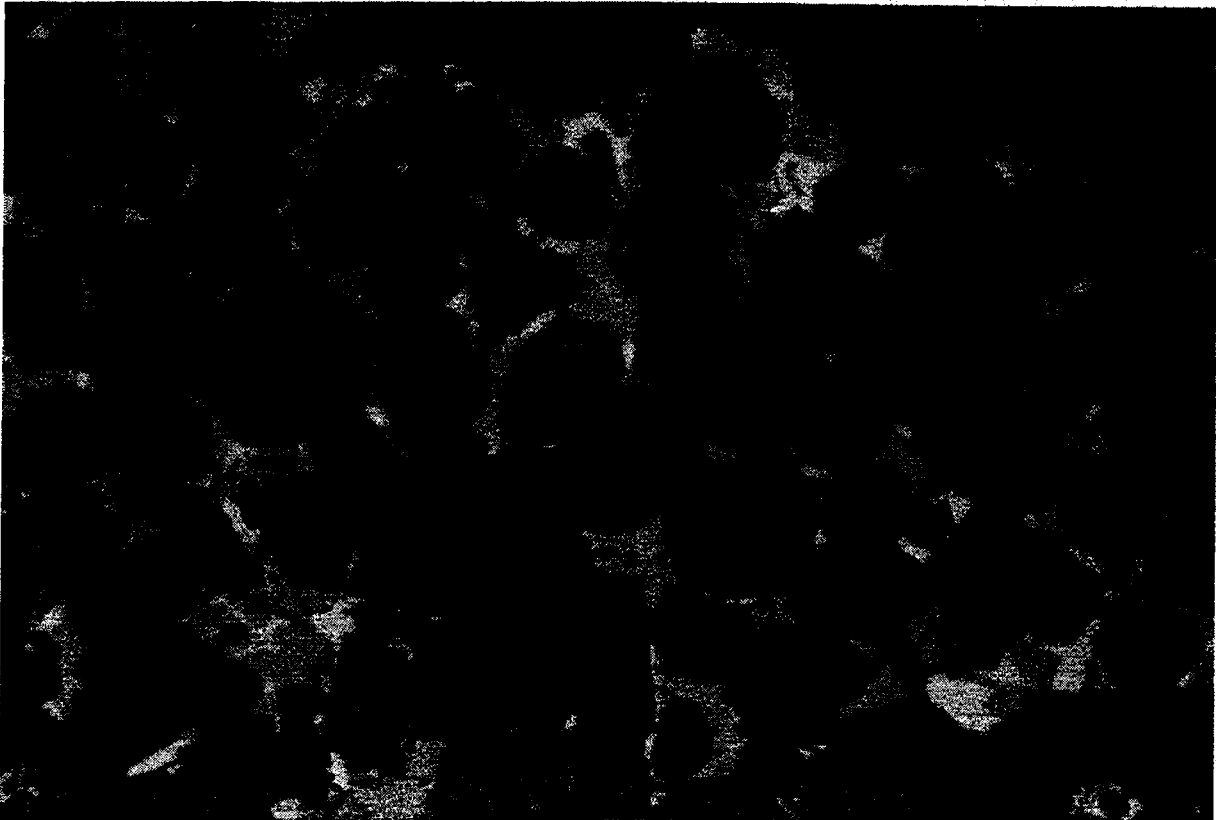
In reality this model exists also in the clinker. Plate 17 shows a clinker with a very inhomogenous distribution of alite, belite and free lime, reflecting directly raw meal inhomogeneity.

**Plate 17      Inhomogeneous distribution of clinker minerals. 64x**



In comparison with the inhomogenous microstructure produced from an inhomogenous raw mix, Plate 18 shows the clinker fabric when the raw mix is correctly homogenized.

**Plate 18 Homogenous distribution of minerals. 250 x**



In comparison with the effects caused by oversize particles, the concentrations areas due to inhomogeneity contain normally more than one clinker component and usually extend over larger areas. Experience shows, however, that a certain clustering, particularly of belite, is almost always observed in plate clinker. The even distribution (Plate 18) is rather an exception.

**2.3.5 Coal Ash**

**Rotary kilns are in ever increasing numbers again being fired using coal.**

Unlike gas and oil, this type of fuel imposes traces of its presence on clinker textures. During the burning of coal, siliceous ash is produced as molten ash drops and these fall as a sediment of the clinker being formed. There is thus a  $\text{SiO}_2$  concentration on the surface of the kiln charge. Depending on how far the ash drops are carried into the kiln, they will be more or less assimilated with the clinker granules. Due to the deposition of ash drops rich in  $\text{SiO}_2$  on the kiln charge, there is a local lack of  $\text{CaO}$ . At these places only belite can be formed and thus the deposition leads to typical belite streaks in the clinker as can be seen in Plate 19. Generally, these streaks are found in the peripheral areas of the pieces of clinker.



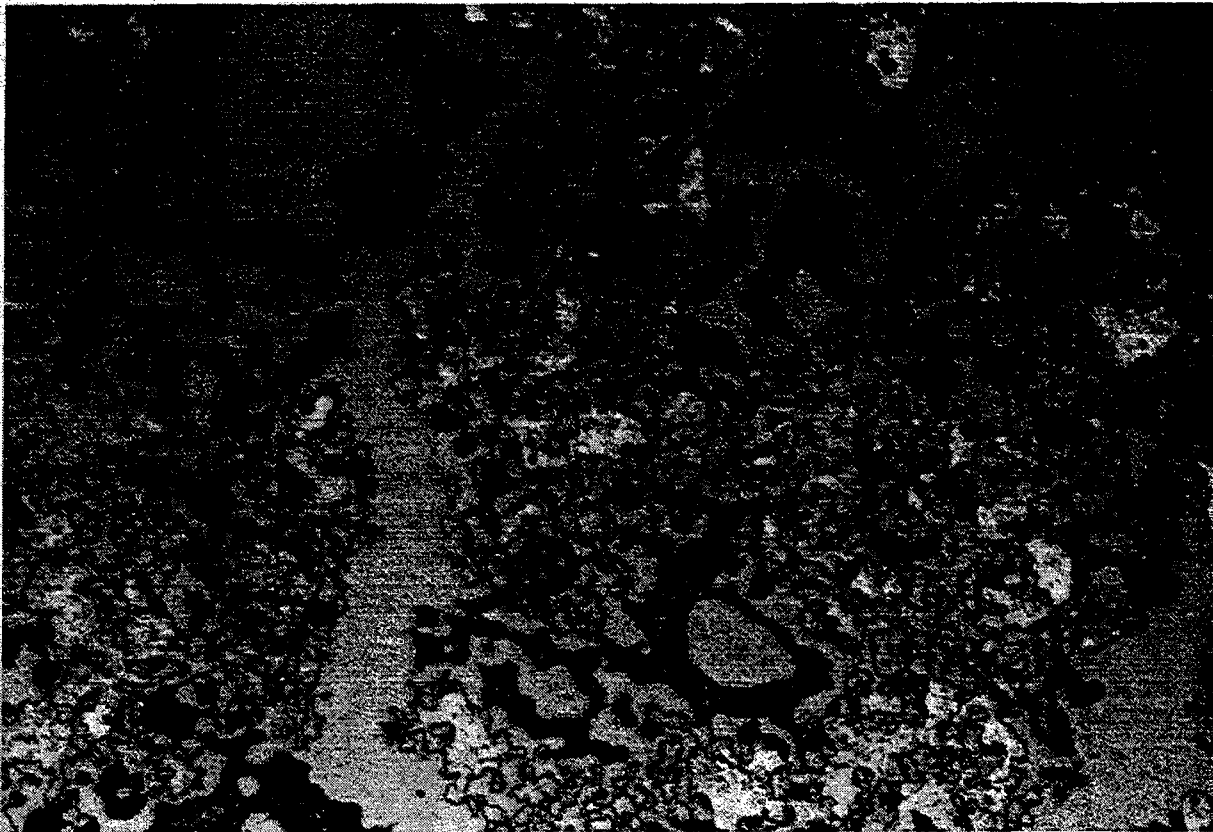
**Plate 19      Belite layer due to coal ash. 64 x**



### 2.3.6 Burning Time / Temperature

Large-scale industrial process conditions do not allow thermodynamic equilibrium to be reached. If the kiln charge passes through the kiln too quickly (flushing) or the sintering temperature is too low (underburning), the same characteristic fabric results as shown in Plate 20.

Plate 20 Underburnt clinker. 64 x



Whether the temperature, the heating time of both parameters were too low cannot be distinguished. As can be seen in Plate 20, the alite and belite crystals are unusually small. Alite is surrounded by large amounts of liquid phase, while belite is concentrated in clusters. In the areas where alite and liquid phase coexist, accompanying free lime appears as a result of uncompleted reaction between lime and silica. High porosity with vesicular cavities in places is also typical.

If all these characteristics are considered, it may be concluded that here the formation of the clinker phases stopped at an early stage. The time and / or temperature was not sufficient to form normal clinker from the raw materials.

Another time - temperature anomaly occurs if the clinker remains in the highest temperature range for too long or if the sintering temperature is too high. Coarsening of the alite and belite grains takes place. It can be shown that the crystallization of calcium silicate also continues during cooling as long as the cooling rate is sufficiently slow. Alite and belite can continue to grow under such conditions - provided that the quantity of the reacting material is large enough - until the liquid phase crystallizes. Therefore, with an extreme crystal growth of calcium silicate, it is not clearly distinguishable if the clinker was over burnt or whether the cooling rate was too slow. **In all these events, hard burning results in clinker of reduced hydraulic activity.**

### 2.3.7 Cooling Rate

**Clinker cooling takes place in two stages, the first cooling stage occurring within the kiln, the second in the clinker cooler.**

The rate of cooling within the kiln depends upon the flame length, on its position in the kiln and on the throughput and speed of the kiln charge. The clinker temperature at the kiln outlet is probably between 1350 and 1200 °C. If the flame is long, this part of the cooling process is very slow and alite and belite can grow to an excessive crystal size. In some cases (when the cooler efficiency is low), alite partially decomposes into belite and free lime (see Plate 4).

The texture of the solidified liquid phase is also very dependent on the cooling rate. During slow cooling, the crystals have time to grow. Ferrite and aluminate form a coarsely grained matrix (Plate 9). Alternatively, if the cooling process proceeds quickly, the opposite takes place, i.e. the crystals are finely grained (Plate 11).

Cooling can also proceed so quickly that the crystals can only form in the sub-microscopic range. Distinction between aluminate and ferrite is no longer possible by microscopy but can be effected by x-ray methods.

## 3. METHODS OF CLINKER INVESTIGATION

### 3.1 Introduction

Investigations on clinker are usually restricted to determining the following properties:

- identification of the minerals
- estimation of the quantity of each species present
- determination of the composition of individual crystals of any single species and hence the composition range of that species
- determination of the habit and spatial distribution (texture) of the minerals.

Several groups of methods are available for the determination of these properties:

- light microscopy, scanning electron and electron microprobe method
- x-ray diffraction
- thermo-analytical methods
- wet-chemical extraction techniques

Often it is necessary to use the combination of these methods if the maximum amount of information or if the highest degree of accuracy is required. No single technique is capable of determining all the desired properties. In Table 4 the normal range of application of each method is listed.

As can be seen, wet chemical methods are certainly capable of being performed at all plants, whereas only a limited number of plants are equipped to perform x-ray diffraction and reflected light microscopy. These latter methods are, however, certainly available in the central laboratory of a group of plants. Investigations using scanning electron microscopy, and an electron microprobe analyzer can only be undertaken by specialized laboratories possessing such advanced and expensive instruments.

**Table 4 Normal application range of the various methods of clinker investigations**

Investigation Method	Clinker properties				Equipment		
	Mineral identification		Mineral composition	Habit / texture	Found in cement plant laboratories	Cost of equipment	Available in TS
	Qualitative	Quantitative					
<b>Microscopy</b>							
Reflected light	+	+	o	+	sometimes	moderate	yes
Scanning electron	o	o	(+)	+	definitely not	very high	no external equipment used
Electron microprobe	+	o	+	o	definitely not	very high	
<b>Diffraction</b>							
<b>X-ray</b>	+	aluminate / ferrite free CaO periclase	ferrite solid solution	o	in a few cases	high*	yes
<b>Wet chemical extraction</b>							
Salicylic acid extraction		alite + belite	o	o	No special equipment required	very low	yes
Glycol extraction		free CaO	o	o		very low	yes
Controlled water extraction		soluble alkali sulfates	o	o		very low	yes

\* except when purchased as an addition for an existing x-ray fluorescence spectrometer

### 3.2 Microscopy and Microprobe Analysis

Cement clinker is, almost without exception, investigated by reflected light microscopy on etched, polished sections. The use of transmitted light microscopy either on thin sections or on powders is rarely practiced.

Great care must be exercised when selecting representative samples, the quantity required depending on the topic under investigation. When information on minerals content, porosity, etc. , is required, the chosen material should be sampled from not only one but from several clinker lumps.

The selected sample is first embedded into a suitable resin (e.g. epoxy resin) to facilitate handling and then treated as follows:

- ground to produce a flat, matt surface (e.g. using carborundum powder)
- polished to obtain a flat, shining surface (e.g. using 0.3 µm diamond paste)
- etched to differentiate between the individual clinker minerals (e.g. using hydrofluoric or acetic acid vapors, or using nitric acid solution).

By using non aqueous grinding and polishing media, the loss of the water soluble alkali sulfates and free lime during sample preparation can be prevented.

### 3.2.1.1 Qualitative mineral analysis

Using the thus prepared polished section it is possible by using magnifications of up to 500 x to determine qualitatively in clinker:

- the minerals present and their habit
- their polymorphic modifications (sometimes)
- clinker fabric (porosity, homogeneity, etc.)

and from this information deduce the influence of such process conditions as:

- fineness of raw mix grinding
- homogeneity of raw feed
- time / temperature of burning
- rate of cooling
- type of fuel used

The use of this method has already been demonstrated in Chapters 2.1, 2.2, 2.3 (see also (4), (5)).

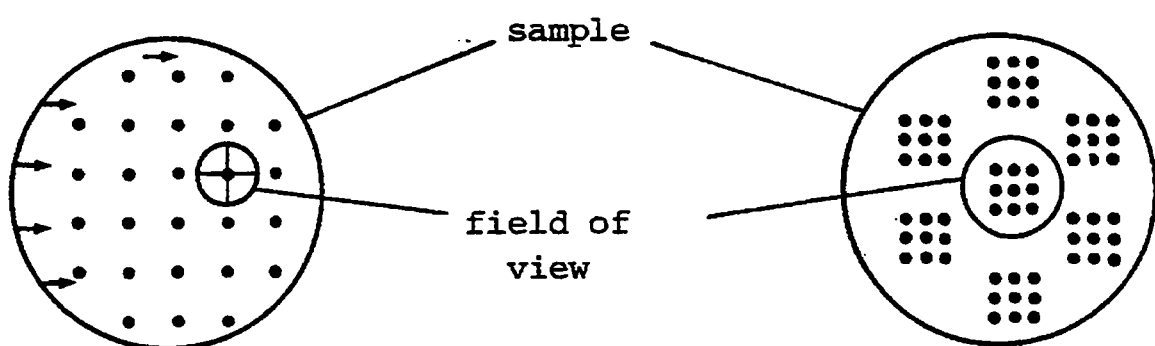
### 3.2.1.2 Quantitative mineral analysis

Clinker properties are **quantitatively** determined by the use of one or two methods, namely:

- ◆ **Linear point counting** i.e. the sample is moved in regular steps and the mineral under the cross-wire is identified and counted.
- ◆ **Area point counting** i.e. a point grid containing 100 points, placed in the microscope ocular, lies apparently over the clinker, and the mineral at each point is counted without moving the clinker. Only after all the points have been counted is the clinker moved to another field of view.

#### Linear point counting

#### Area point counting



Both methods determine the area percent of the minerals in the polished section, and to convert the results into weight percent, the following mineral densities ( $\text{g/cm}^3$ ) must be taken into account:

alite	3.20	belite	3.28	aluminate	3.04
ferrite	3.77	periclase	3.58	free lime	3.30

To obtain a high accuracy, the TS/MA counts 4000 points (N), giving an absolute statistical counting error ( $\delta$ ) at the 95 % confidence level of

$$\delta = 1.96 \sqrt{\frac{P(100 - P)}{N}}$$

P = % points for the counted minerals

The most usual features to be quantitatively determined include:

- clinker mineralogy
- size distribution of minerals (is related to hydration reactivity)
- homogeneity
- porosity

Whereas the Bogue formula calculates the **potential** quantities of minerals present, microscopical analysis determines the quantities **actually present**. The difference between both methods has already been demonstrated in Chapter 1.4.2 for alite and belite.

### 3.2.2 Scanning Electron Microscope Analysis

By using a fine electron beam in place of light in such a way that the beam scans the sample surface in a raster pattern, it is possible to obtain an optical image of the surface on a TV screen. This image can have a magnification of up to 10,000 x, combined with a **good depth of focus**. By further increasing the magnification (up to 100,000 x) the quality of the image is reduced.

Using the **energy disperse x-ray spectrometry** technique (EDAX), it is now also possible to determine semi-quantitatively the chemical composition of the observed minerals.

Examples of clinker investigated by scanning electron microscopy are displayed in Plates 21 - 24.

**Plate 21**      **Idiomorphic alite (A) embedded in sulfate-rich matrix (S). 2000 x**



**Plate 22 Alite (A) and belite (B) in sulfate-rich matrix (S). 2000 x**

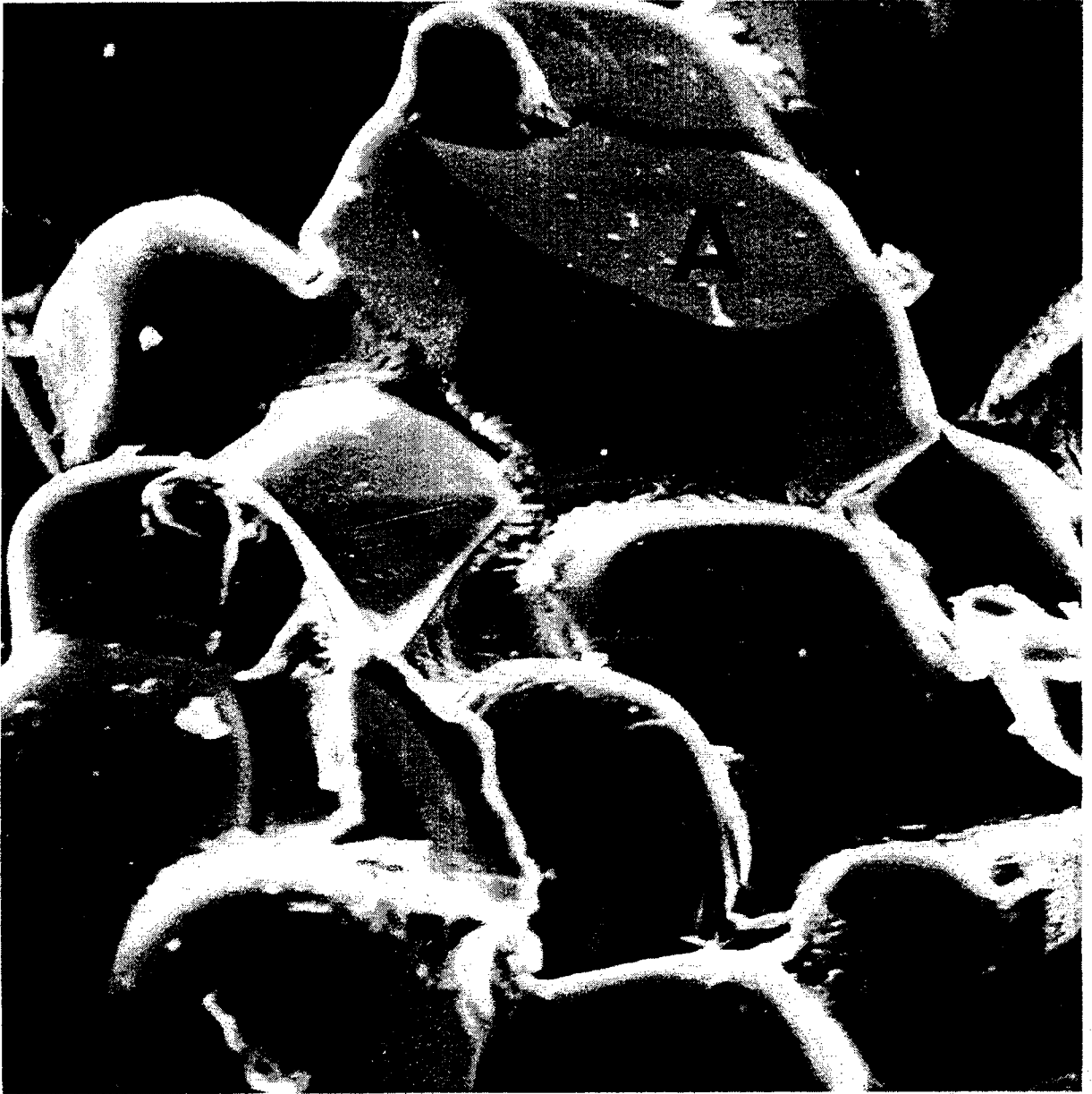
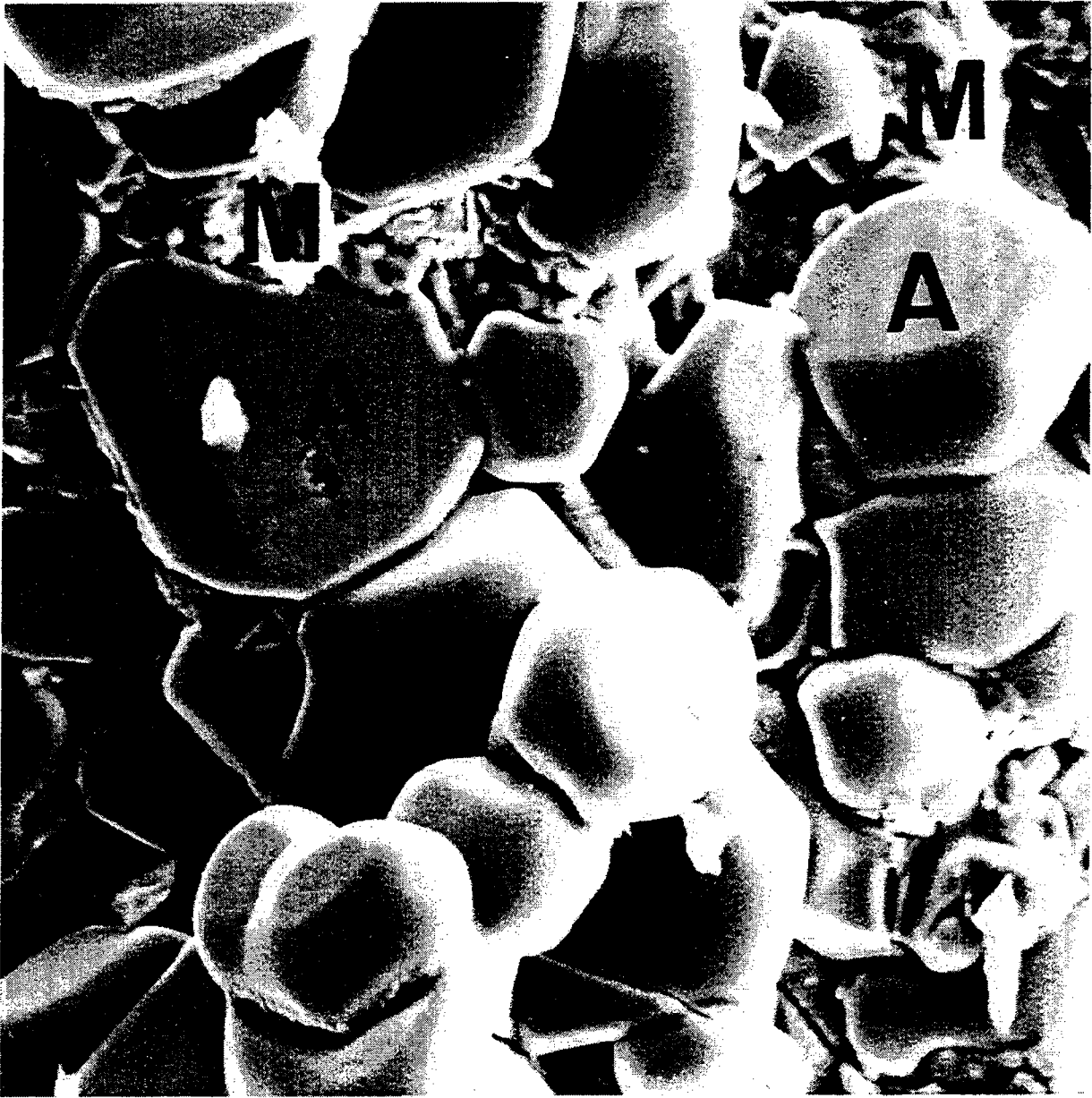
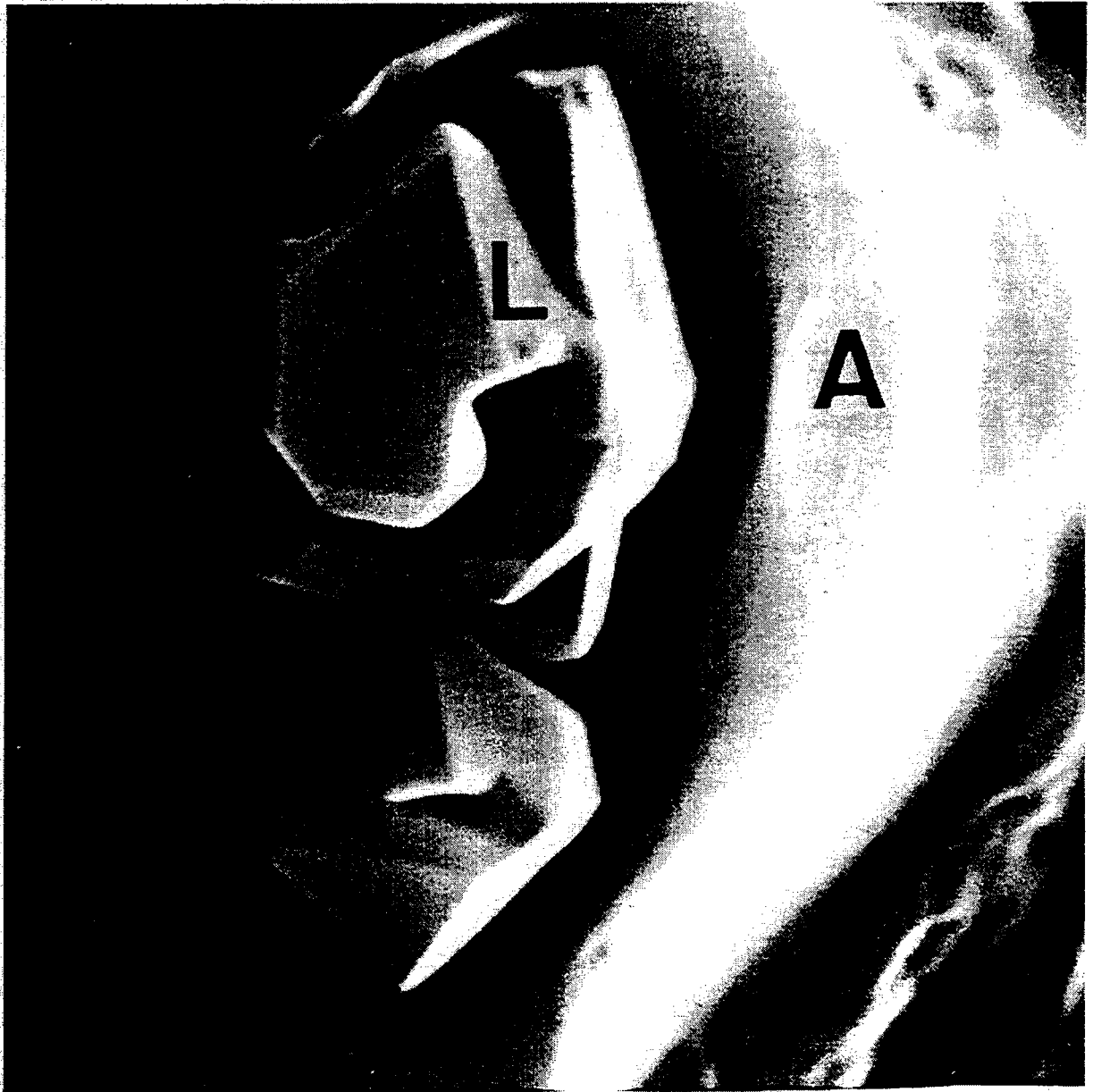


Plate 23 Alite (A) in aluminite / ferrite matrix (M). 2000 x





**Plate 24** Free lime (L) in contact with alite (A). 9500 x



### 3.3 X-ray Powder Diffraction

#### 3.3.1 Methodical

The examination of clinker by x-ray powder diffraction can with much experience be used to determine:

- the minerals present - quantitative and qualitative
- their polymorphic modification (s)
- the approximate composition of certain minerals

The full potential use of the method as a basic routine technique, however, is made difficult by the following:

- variations in the chemical composition of almost all minerals
- more than one modification of the same mineral almost always present
- the x-ray intensities of the various modifications are not equal
- overlapping of various reflections and small concentrations require pre-preparation of the sample by wet chemical extraction
- the relatively high cost of the equipment. This can be somewhat reduced when x-ray diffraction facilities are combined with existing x-ray fluorescence equipment.

#### 3.3.2 Experimental Technique

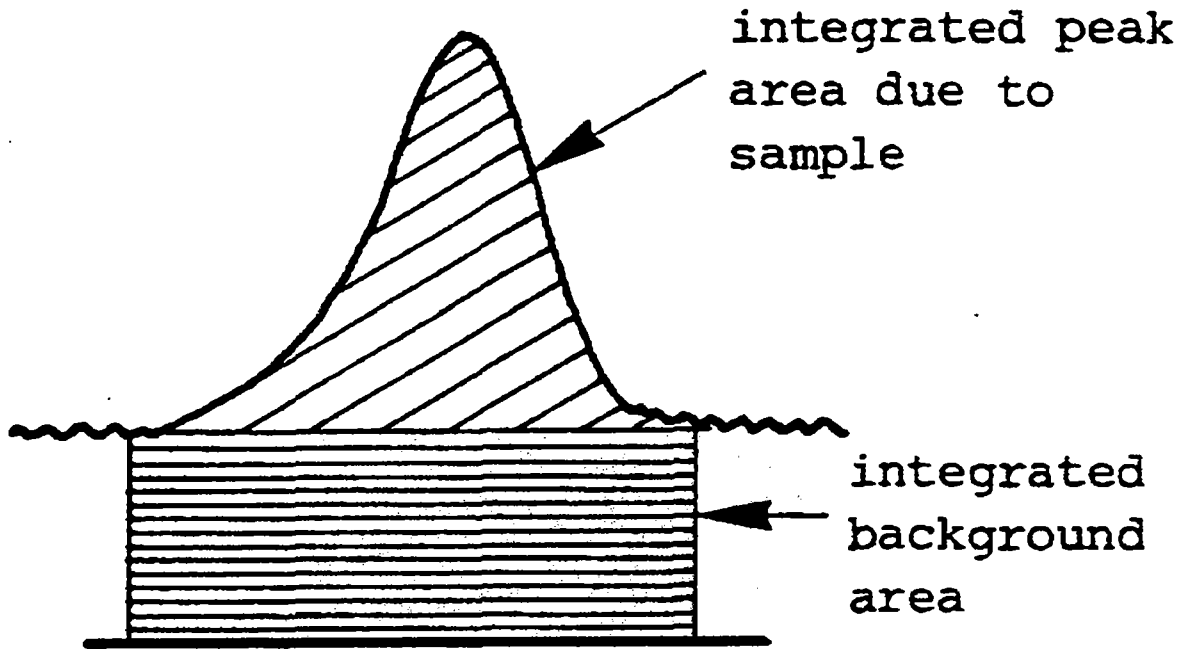
Samples to be investigated must be finer than 20  $\mu\text{m}$  when determinations are desired. The prepared sample is then irradiated in a focused x-ray beam (e.g. Cu or Cr radiation) and the characteristic peaks of each mineral recorded.

For **qualitative** analysis the  $2\theta$  values of the peaks are compared with the characteristic peaks of the known clinker minerals and in this way the following can be determined:

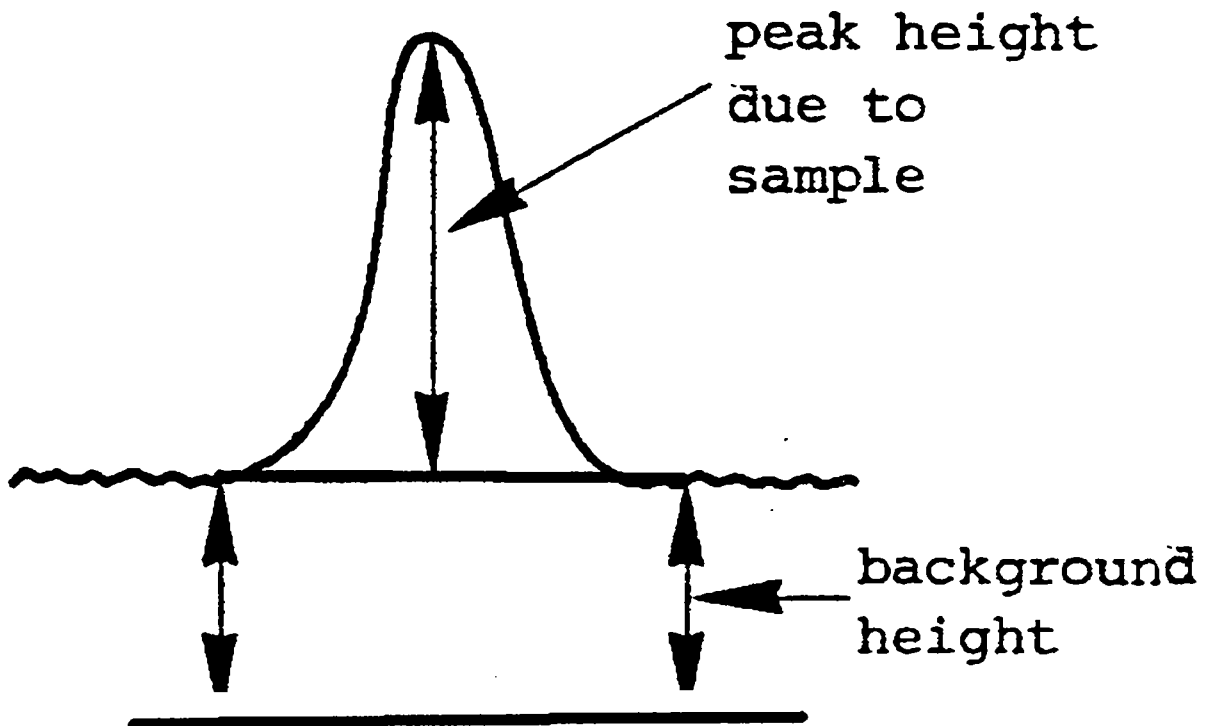
- the presence and polymorphic modifications of alite, belite
- the presence and solid solutions of aluminate and ferrite
- the presence of  $\text{MgO}$ ,  $\text{CaO}_{\text{free}}$

For **quantitative analysis**, suitable strong reflections of the required minerals, free of interference from other mineral peaks, are required. As measurement criterion either the effective **peak height** or **integrated peak area** may be applied, this being obtained by subtracting the background radiation level from the **overall** peak height or peak area.

#### **Peak area method**



Peak height method



Two types of calibration can be applied in which the measured effective peak area or height is compared to that of either an **internal** or **external** standard (e.g.  $\text{SiO}_2$ ,  $\text{CaF}_2$ ,  $\text{TiO}_2$ ).

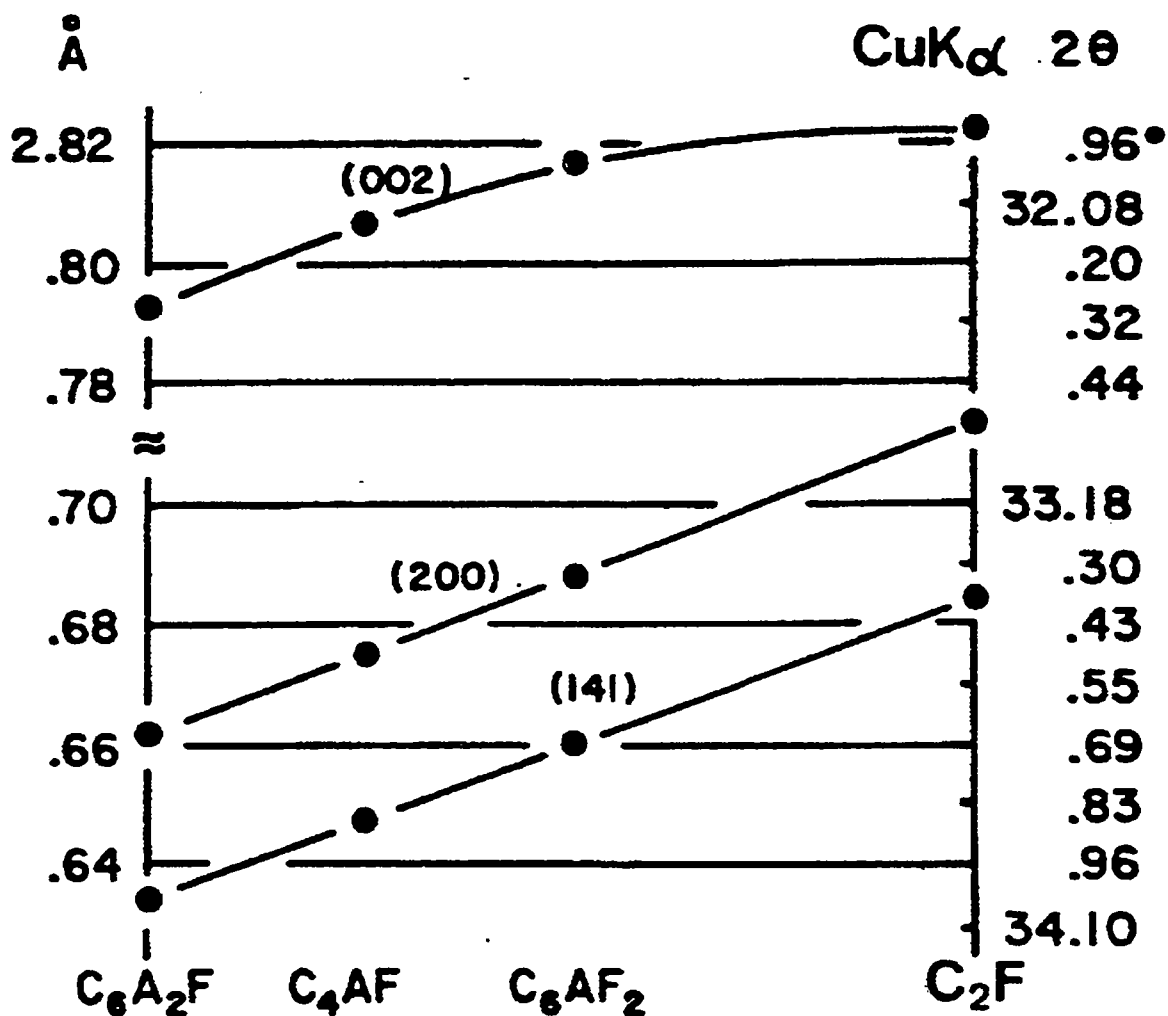
The **external standard** method, i.e. standard and sample not mixed together, eliminates errors due to fluctuations in the equipment itself. (e.g. instability of x-ray generator, x-ray counter, etc.), but makes no allowance for changes in material parameters (e.g. absorption by matrix). This latter effect can be compensated for by employing an **internal standard**, i.e. by mixing the standard powder **into** the powder being investigated.

3.3.3 Applications of x-ray diffraction

Determination of ferrite solid solution

As mentioned previously, the ferrite composition is only approximately  $C_4AF$ . The true solid solution present in clinker can, however, be determined using x-ray diffraction, employing the change in the  $2\theta$  value of characteristic peaks as evaluation criterion. The latter are shown in Figure 13.

Figure 13 Change of peak reflections (002, 200, 141) for ferrites in the  $C_2F$ ,  $C_6A_2F$  series.



A useful application of knowing the actual ferrite composition is, that it can be used to obtain a better Bogue formula estimation of aluminate and ferrite than the one obtained by assuming the composition to be  $C_4AF$ .

### **Determination of free lime**

By extending x-ray fluorescence facilities to include x-ray diffraction (at a fraction of the cost for x-ray diffraction alone), it is possible to quickly and accurately measure free lime as a process control method, avoiding the use of glycol extraction. The main advantage of the x-ray method is the reduced time required (10 minutes) using the same sample prepared for x-ray fluorescence. Free lime values in the range 0.5 - 5 % can be determined at an accuracy of  $\pm 0.3$  %  $\text{CaO}_{\text{free}}$  at the 95 % confidence level.

For the determination of other, more complicated clinker analyses (e.g. quantitative determination of the clinker minerals), it is highly recommended that contact be first established with the TS/MA or other suitable qualified laboratories.

### **3.4 Clinker Analysis by Wet Chemical Extraction Method**

When neither microscope nor x-ray facilities are available, certain minerals or groups of minerals can still be quantitatively determined by selective extraction using wet chemical methods.

Minerals which can be quantitatively determined to an acceptable degree of accuracy by such inexpensive but rather limited techniques include:

**Alite + belite + free CaO:** using ethanolic salicylic acid

**Free lime and  $\text{Ca(OH)}_2$ :** using ethylene glycol extraction. The proportion of free lime alone can be ascertained by subtracting the  $\text{Ca(OH)}_2$  value determined via its  $\text{H}_2\text{O}$  loss on thermal decomposition

**Alkali and alkali/calcium sulfates:** by controlled extraction with  $\text{H}_2\text{O}$  and determination of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{SO}_3$  levels in the extracted solution

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